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Marciniak, Aryane A., Lamb, Katie J. orcid.org/0000-0002-5244-5015, Ozorio, Leonardo P. et al. (2 more authors) (2020) Heterogeneous catalysts for cyclic carbonate synthesis from carbon dioxide and epoxides. Current Opinion in Green and Sustainable Chemistry. 100365. ISSN 2452-2236

https://doi.org/10.1016/j.cogsc.2020.100365

Heterogeneous catalysts for cyclic carbonate synthesis from carbon dioxide and epoxides

Aryane A. Marciniak[1], Katie J. Lamb[2*], Leonardo P. Ozorio[1], Claudio J. A. Mota[1,3,4*], Michael North[2]

[1] Universidade Federal do Rio de Janeiro, Escola de Química. Av. Athos da Silveira Ramos 149, CT Bl E, 21941-909, Rio de Janeiro, Brazil.

[2] The University of York, Department of Chemistry, Green Chemistry Centre of Excellence, Heslington, YO10 5DD, York, United Kingdom.

[3] Universidade Federal do Rio de Janeiro, Instituto de Química. Av. Athos da Silveira Ramos 149, CT Bl A, 21941-909, Rio de Janeiro, Brazil.

[4] INCT Energia e Ambiente, UFRJ, 21941-909, Rio de Janeiro, Brazil.

Corresponding authors: katie.lamb@york.ac.uk, cmota@iq.ufrj.br, michael.north@york.ac.uk

Abstract

This review surveys six classes of heterogeneous catalysts that have been used in the conversion of epoxides and CO_2 into cyclic carbonates; metal organic frameworks (MOFs); silica-based catalysts; organic polymer supports; metal oxides; zeolites and carbon-based catalysts. Many of these catalysts are extremely active in the ring-opening of terminal epoxides, require fairly mild conditions and can be made in a sustainable manner. Some catalytic systems however require toxic and hazardous chemicals in their synthesis, and many struggle to ring-open the more sterically demanding and hindered internal epoxides. This review covers the most recent heterogeneous catalysts reported in the literature, not only from a catalytic efficiency perspective but also from a green chemistry and sustainable viewpoint.

Keywords: carbon dioxide, catalysts, epoxides, cyclic carbonates, heterogeneous catalysis

1. Introduction

Carbon dioxide (CO_2) is a major anthropogenic greenhouse gas, produced by the chemicals, thermoelectric and steel industries and by the

transportation sector. Global CO_2 emissions have created many environmental issues, such as climate change and global warming. In order to try and reduce our emissions, many researchers are focused on performing sustainable carbon dioxide capture and storage (CCS) [1] and carbon dioxide utilisation (CDU) [2].

Carbon dioxide is an abundant, inexpensive and non-toxic chemical feedstock. However, CO_2 is also thermodynamically stable (ΔH_f = -393.5 kJ/mol) [3]. Research into developing efficient catalytic systems to overcome the large energy barriers often associated with reactions of CO_2, in order to convert CO_2 into commercially viable products for the chemical industry, is therefore an important area of research. One popular group of chemicals that can be made from CO_2 are organic carbonates, and in particular cyclic carbonates.

Cyclic carbonates are valuable industrial raw materials with a wide range of applications, including: alternative polar aprotic solvents, electrolytes in lithium-ion batteries, polymer precursors and fuel additives. They are also vital organic intermediates in the production of pharmaceutical, agricultural and fine chemicals, such as dialkyl carbonates, glycols, carbamates, pyrimidines and purines (Figure 1) [4,5].

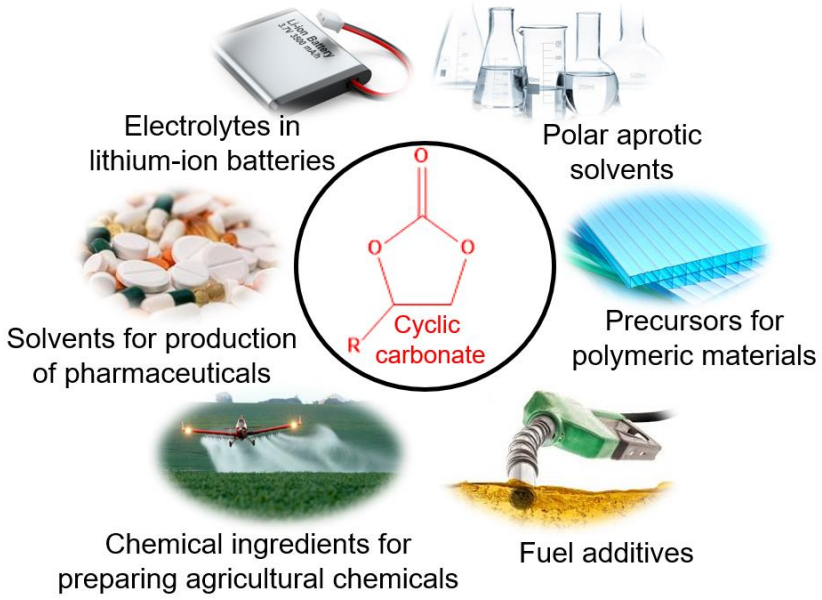


Figure 1. Important industrial applications of cyclic carbonates [5–7].

Cyclic carbonates can be produced directly by the catalyzed, 100% atom economical reaction between an epoxide and CO_2. Alternatively they can be

made by catalyzed or uncatalyzed condensation reactions between a diol and CO_2, or an activated form of CO_2 such as urea or dimethyl carbonate, both of which can in turn be prepared from CO_2. The direct reaction between epoxides and CO_2 is by far the more studied approach and many catalysts have been developed for this reaction. A large number of homogeneous catalysts, including phosphines, quaternary onium salts, transition metal complexes and alkali metal salts, have been used, as they can enable the reaction to occur under mild conditions, sometimes at room temperature and atmospheric pressure [8]. However, problems associated with homogeneous catalysts, such as removing the catalysts from the reaction mixture post-reaction, and recycling the catalyst, have encouraged researchers over the last few decades to develop heterogeneous catalysts.

Recently, six classes of heterogeneous catalysts have been used to transform CO_2 into cyclic carbonates: metal organic frameworks (MOFs); silica-based catalysts; organic polymer supports; metal oxides; zeolites and carbon-based catalysts. Each of these groups will be reviewed and discussed, with a special emphasis on the sustainability and “greenness” of the catalysts and reaction procedures.

2. Heterogeneous catalysts

2.1. Silica-based catalysts

Amine-functionalized silica materials, possessing organo-basic sites on the surface and acidic metal or silanol groups with the material framework, have been researched as catalysts for cyclic carbonate formation. These species are attractive catalysts, as the presence of the acidic silanol hydroxyl groups can facilitate the ring-opening of an epoxide. Furthermore, many authors propose that the basic moieties (for example amine groups) may activate the CO_2 molecule, thus making it more reactive.

In 2017, Ahmed and Sakthivel investigated the synthesis of organo-amine functionalized chabazite (CHA)-type silicoaluminophosphate (SAPO-34) materials, via an *in situ* approach using hydrothermal conditions [9]. Ahmed and Sakthivel’s research studied the functionalization of CHA-type SAPO-34 (S-34-xN) materials with different concentrations of 3-aminopropyltrimethoxysilane

(0.16 to 0.64 M), which were called S-34-0.16N, S-34-0.24N, S-34-0.32N, S-34-0.40N and S-34-0.64N. These functionalized materials exhibited promising catalytic activity with high epichlorohydrin (ECH) conversions (>80%) and selectivity to cyclic carbonate (>94%), in 5 hours using 0.64 M of immobilized amine, 6 bar of CO_2 at 85 °C and using 0.2 g of catalyst with 30 mmol of ECH. Furthermore, the S-34-0.64N catalyst showed the best catalytic activity and stability, and could be used up to four times in converting ECH into cyclic carbonate. The authors reported that incorporating basic amine sites into the catalysts overall played a crucial role in CO_2 activation on the catalyst surface (Step I, Figure 2), while the acidic sites of the SAPO-34 framework accelerated epoxide ring-opening (Step II, Figure 2). This has also been reported for similar silica-based catalysts in the literature.

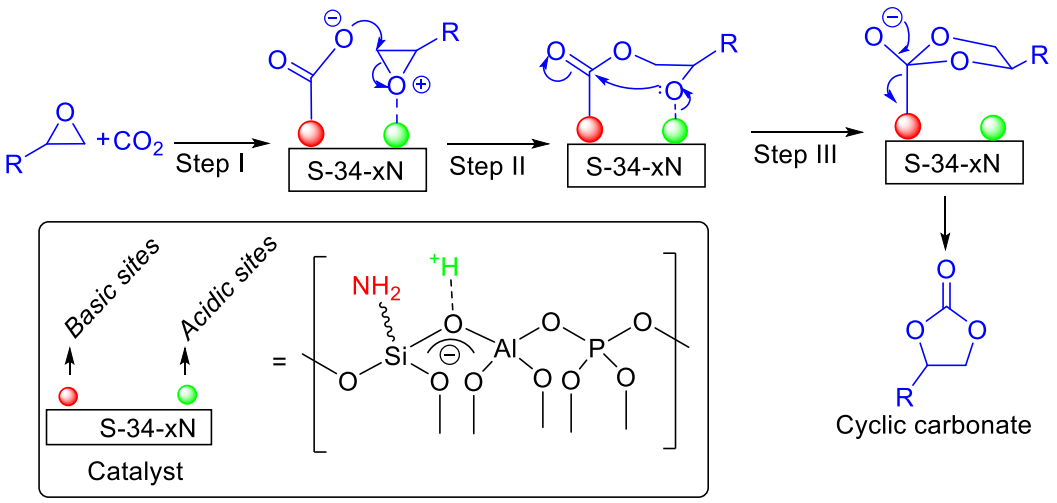


Figure 2. Schematic proposal for cycloaddition of CO_2 and epoxides using S-34-xN as catalyst [9].

In light of Ahmed and Sakthivel's promising work, in 2018, Yamasaki *et al.* [10] synthesized a methylated nitrogen-substituted mesoporous silica SBA-15 material (MeNSBA-15), which was a promising catalyst for the synthesis of cyclic carbonates from CO_2 and propylene oxide (PO). This material could be used without a high temperature pretreatment/activation step. It was also discovered that methylation enhanced the nucleophilicity of the basic nitrogen atoms in the catalyst, increasing the Turn Over Frequency (TOF) considerably from 1.0×10^{-3} h^{-1}, for the non-methylated nitrogen substituted catalyst (NSBA-

15), to 6.4 h^{-1}, using MeNSBA-15 as the catalyst. The selectively to propylene carbonate (PC) was >99%, using 30 bar of CO_2, 14 mmol of PO and 0.1 g of catalyst at 100 °C for 3 hours.

Using kinetic analysis experiments, the authors showed that the methylated *N*-substituted heterogeneous catalyst (MeNSBA-15) reacts with epoxides and CO_2 via a Langmuir–Hinshelwood mechanism. This mechanism suggests that the incorporation of epoxide occurs at a basic amine site, followed by the ring-opening step; whilst the CO_2 is adsorbed on another amine site, followed by a bimolecular reaction occurring between the ring-opened alkoxide intermediate and carbamate over neighboring methylated nitrogen sites. In this case, both CO_2 and the epoxide are adsorbed onto the active sites near the silanol group of MeNSBA-15, which will act as a weak Lewis acid site and synergistically stabilize the alkoxide intermediate.

Following on from Yamasaki's work, in 2019, Liu *et al*. [11] synthesized an amorphous mesoporous titanium silica-based material, using poly(diallyldimethylammonium) chloride (PDDA) as the mesopore template. The authors reported that this material acted as an efficient multi-functional catalyst for reacting CO_2 with epoxides, as the organic species (PDDA) embedded in the mesoporous channels can act as a Lewis base, and cooperate synergistically with the Lewis acidic titanium ions (Ti^{4+}) in the reaction mechanism. Thus, the presence of PDDA, which increased the number of basic sites in the catalyst, leads to an efficient heterogeneous bifunctional catalyst for cyclic carbonate formation, presenting both high ECH conversion (96.5%) and cyclic carbonate selectivity (95%), under the optimum reaction conditions (0.4 g of catalyst and 30 mmol of ECH at 16 bar of CO_2 and 120 °C for 6 hours).

It was proposed in the reaction mechanism (Figure 3), that the basic nitrogen groups activate the CO_2 molecule (Step 1, Figure 3) and, analogously, an acidic metal Ti^{4+} site activates the oxygen atom of the epoxide (Step 2, Figure 3). The nucleophilic carbamate anion (Step 3, Figure 3) then attacks the less hindered carbon of the epoxide, leading to epoxide ring-opening, followed by generation of cyclic carbonate (Step 4, Figure 3).

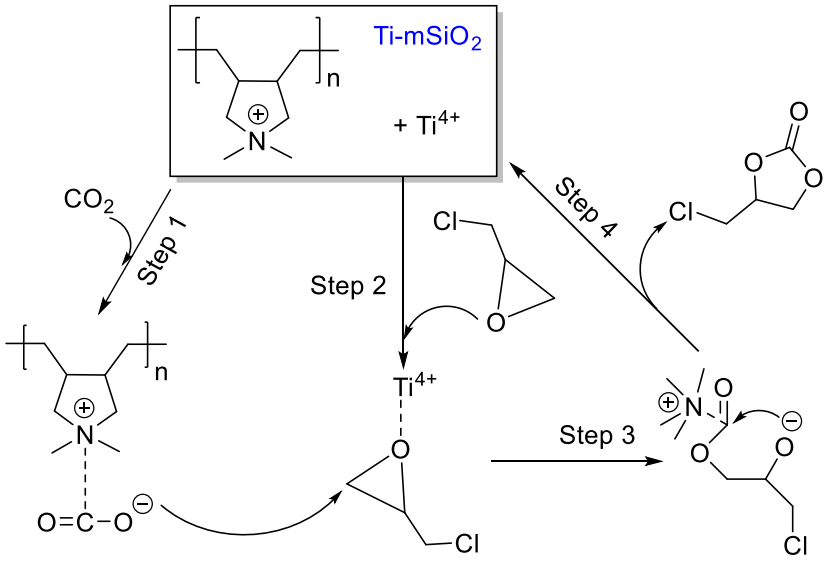


Figure 3. Proposed reaction steps for the cycloaddition of CO_2 and ECH using Ti-mSiO_2 as catalyst [11].

In the same year, Liu and co-workers developed zwitterionic nanocatalysts with imidazole-urea derived frameworks [12]. The imidazole-urea components were attached to mesoporous hybrid silica materials, and different versions of the catalyst with various nucleophilic anions were prepared (Figure 4).

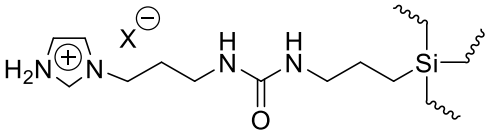


Figure 4. Zwitterionic nanocatalyst. X= (Cl, Br, I, NO_3) [12].

The authors reported that the catalytic activity for synthesizing PC from PO and CO_2 was influenced by anion nucleophilicity, with an activity trend of I > Br > Cl > NO_3 [12]. By using 5 wt% of iodide as the anion in the catalyst (Im-Si-I-5), PC was produced under mild conditions in high yield (96%) and selectivity (99%), without a co-catalyst or solvent. The recyclability of this catalyst was measured and no significant drop in cyclic carbonate yield was observed after 4 uses using the optimum reaction conditions (110 °C and 25 bar of CO_2 for 4 hours using 7.5 wt% of Im-Si-I).

As shown by Yamasaki *et al*. [10] in 2018, functionalized SBA-15 is an effective material for cyclic carbonate synthesis, due to its high surface area, high hydrothermal and mechanical stability, acidic silanol groups and uniform pore structure [13]. Following on from this research, many heterogeneous catalysts based on SBA-15 were developed in 2019. One example is the triethanolamine (TEA)-modified mesoporous SBA-15 catalyst, reported by Zhang *et al*. [14], which has been widely used as a CO_2 adsorbent due to its high basicity. It was found that using 2 g of TEA on the SBA-15 solid support (termed as TEA(2.0)/SBA-15), the yield of PC increased (94%) compared to using SBA-15 alone, with high PC selectivity (99%) under mild conditions (20 bar of CO_2, 110 °C for 4 hours using 0.2 g of catalyst with 34.5 mmol of PO).

Reusability tests found that TEA(2.0)/SBA-15 exhibited excellent yields (>90%) after 5 cycles under the same conditions, thus highlighting the stability of the catalyst. The mechanism proposed by Liu *et al*. [12] and Zhang *et al*. [14] does not follow the Langmuir–Hinshelwood mechanism, i.e. the CO_2 molecule is not adsorbed on the basic sites. Instead, the CO_2 attacks the oxyanion intermediate, produced by the iodide ring-opening the epoxide, thus leading to cyclic carbonate formation (Figure 5).

Zhang *et al*. [15] investigated the use of novel amine-incorporating benzene-bridging organosilica nanotubes (AM_x-NT), where x is the molar fractions of 3-aminopropyltrimethoxysilane (APTMS) incorporated in the nanotube, to catalyze the cycloaddition of CO_2 to epoxides. By using the $AM_{0.4}$-NT catalyst, with a pore diameter and length of 7 nm and 60 nm, respectively, in presence of tetrabutylammonium iodide (TBAI, *n*-Bu_4NI), fast conversions of PC (TOF = 80 h^{-1}) were achieved under mild conditions (10 bar CO_2, 70 °C for 10 hours using 1 mol% of TBAI).

The NH_2 group was proposed to act as a basic site, which firstly activates CO_2 and then facilitates the coupling of the activated CO_2 with the ring-opened intermediate, forming a carbonate intermediate. The results show that the basic amine groups function effectively with the acidic silanol groups to create an effective bifunctional catalyst.

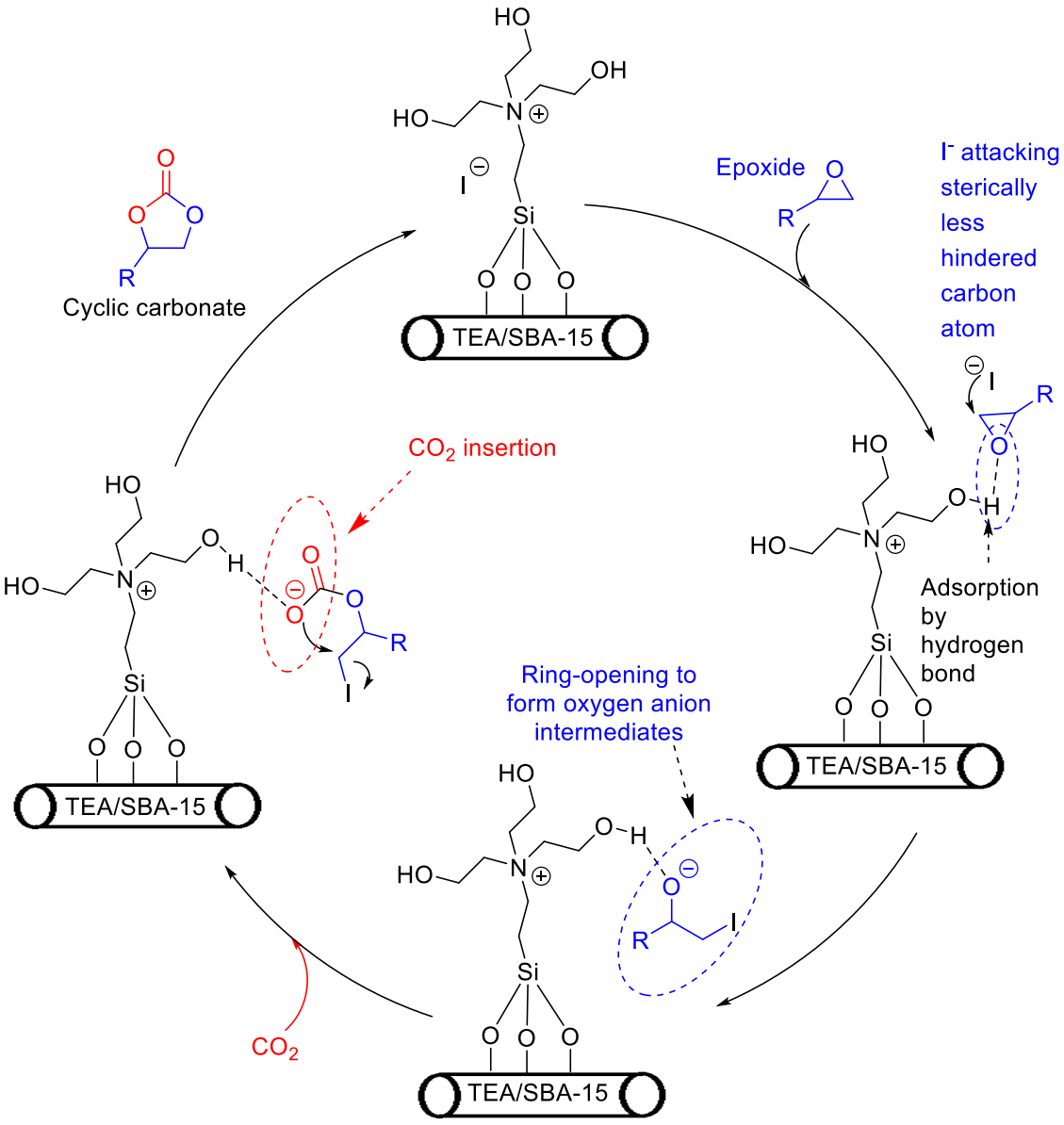


Figure 5. Schematic proposal for cycloaddition of CO_2 and epoxides using TEA/SBA-15 as catalyst [14].

2.2. Metal Organic Frameworks (MOFs)

MOFs are organic–inorganic hybrid porous materials, which have been demonstrated to be promising catalysts for cyclic carbonate synthesis. The porosity and the Lewis acidic sites (unsaturated metal cations) make MOFs ideal candidates for epoxide activation [16,17]. A serious drawback, which limits the application of MOFs however, is the poor availability and accessibility of active sites. Several well-known MOFs, including MIL-101, UiO-66, MOF-892 and ZIF-95 [18–21] have shown low catalytic activity due to a lack of functional

sites, especially basic sites. It is therefore often necessary to use Lewis basic co-catalysts with MOFs, to synthesize cyclic carbonates.

The majority of studies have focused on using a quaternary ammonium salt, for example *n*Bu_4NX (where X= Br^- or I^-) as a co-catalyst, because of their highly synergistic effect with MOFs. The generally accepted reaction mechanism for the cycloaddition of CO_2 with epoxides using MOFs and a co-catalyst first involves activation of epoxide, followed by the epoxide ring-opening and then CO_2 insertion to form a cyclic carbonate (Figure 6).

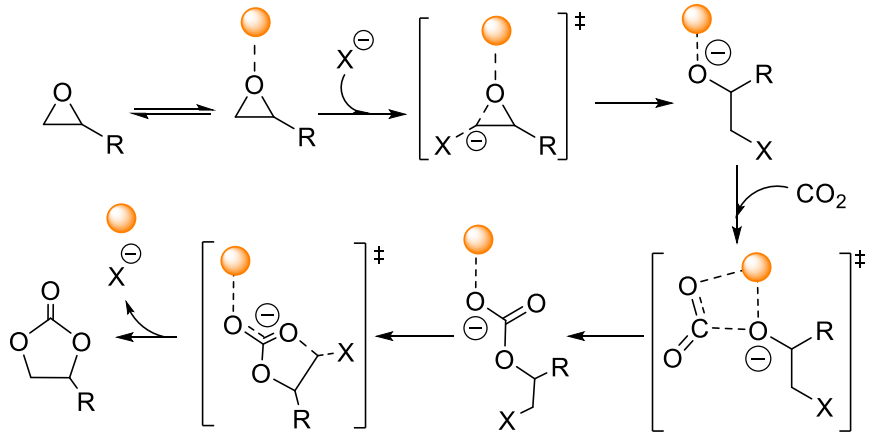


Figure 6. The generally proposed mechanism of cyclic carbonate synthesis from CO_2 and epoxides using heterogeneous MOF catalysts. The orange sphere represents the acidic metal center and X represents the halide anion of the co-catalyst.

In 2017, Xue *et al*. [22] reported the use of gadolinium (Gd), a rare-earth-metal to make a Gd-MOF catalyst ($Gd_2C_{15}H_3O_{36}$) as a heterogeneous catalyst for the cycloaddition of epoxides and CO_2 in the presence of quaternary ammonium salts. Various quaternary ammonium salts were tested (*n*-Bu_4NBr, *n*-Pr_4NBr, Et_4NBr, Me_4NBr, *n*-Bu_4NCl, *n*-Pr_4NCl, Et_4NCl and Me_4NCl). It was found that $Gd_2C_{15}H_3O_{36}$ combined with *n*-Bu_4NBr gave the highest yields for converting ECH into cyclic carbonate (99.1%) under mild reaction conditions (20 bar of CO_2, 80 °C for 5 hours using 0.1 g of catalyst and 2.5 mol% of *n*-Bu_4NBr with 20 mmol of ECH). The use of the rare metal gadolinium in this catalyst is however not ideal from a green chemistry and sustainability perspective.

In 2017, Li *et al*. [23] imbedded the nontoxic Sr^{2+} ion into a new MOF catalyst, as a promising alkaline Earth metal and strong Lewis acid active site. The authors reported that the bromide anion of tetrabutylammonium bromide

(TBAB, *n*-Bu_4NBr) effectively ring-opens the epoxide, generating a high PO conversion (98.5%) and turnover number (TON, 117.4 $mmol_{product}/mmol_{catalyst}$). Conversions and TON were lower when no TBAB was used in the reaction mixture (PO conversion of 5.9% and TON of 7 $mmol_{product}/mmol_{catalyst}$), illustrating the importance of the co-catalyst. The optimum reaction conditions were extremely mild, requiring only 1 bar of CO_2 at room temperature for 48 hours. In the same year, Lu *et al*. [24] also reported the use of TBAB as an efficient co-catalyst with the Cd(III)-MOF catalyst $[(CH_3)_2NH_2]_6[Cd_3L(H_2O)_2]\cdot 12H_2O$, which was synthesized via solvothermal assembly of resorcin[4]arene-functionalized dodecacarboxylic acid ($H_{12}L$) and Cd(II) cations. The isolated yields reported in converting ECH, under mild reaction conditions, increased from 41 to 88%, when the co-catalyst TBAB (0.5 mmol) was added to the reaction mixture.

In 2018, Lan *et al*. [25] compared catalytic activity between a simple MOF catalyst and a zinc based MOF-Zn-1 ($Zn_2L_2MA\cdot 2DMF$) with TBAB, where MA is melamine and H_2L is 2,5-thiophenedicarboxylic acid. Similar to Lu's work, the authors reported that bromide is important for the reaction mechanism. Noh *et al*. [16] showed that the non-functionalized pristine UiO-66 catalyst, which consists of $Zr_6O_4(OH)_4$ SBU (secondary building units) and 12 BDCs (benzene-1,4-dicarboxylates, Figure 7), gave a good yield of PC (77% at 50 °C), using TBAI as co-catalyst under 10 bar of CO_2 for 12 hours with 1 mol% of co-catalyst and 2 mol% of catalyst. The catalytic efficiency of UiO-66 without TBAI was very low (24%).

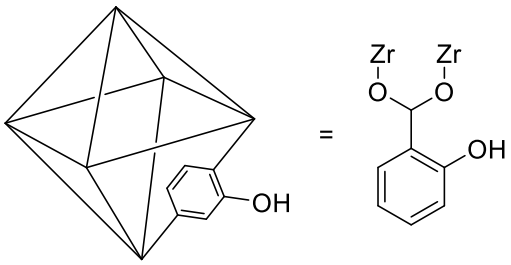


Figure 7. Simplified structure of the UIO-66 Zn-based catalyst [25].

In the same year, two amino-acid-based MOFs containing copper and zinc respectively, were reported by Jeon *et al*. [26] and Kim *et al*. [27]. Both catalysts showed excellent ECH conversion (>90%) with TBAB as a co-catalyst, under the optimized reaction conditions (80 °C, 1 mol% of catalyst, 6 h and 12

bar of CO_2). In both papers, the authors reported that the reactions were performed under solvent-free conditions, which is advantageous from a green chemistry perspective. In 2019, many authors reported the use of MOFs and co-catalysts as efficient systems for cyclic carbonate formation as summarized in Table 1.

Table 1. Summary of MOF-based catalytic systems reported in cyclic carbonate synthesis.

Catalyst	Co-catalyst	Reaction conditions	Conversion (%)	TON[a]	Selectivity (%)	Ref.
Cu-MOF1	TBAB	25 bar, 5 h, 80°C	99 (yield)	-	-	[28]
MOF1	TBAB	1 bar, 24 h, RT	100	200	-	[29]
MOF-5	TBAB	4 bar, 4 h, 50 °C	93	720	-	[30]
Ni-MOF-1	TBAB	1 bar, 6 h, 60 °C	94 (yield)	37.6	-	[31]
MOF-5-MIX	TBAB	12 bar, 6 h, 50 °C	98	-	99	[32]
UiO-66	TBAB	12 bar, 8 h, 60 °C	67	-	>99	[33]
Cu-BTC (BTC = benzene-1,3,5-tricarboxylate)	TBAB	12 bar, 8 h, 60 °C	78	-	>99	[33]
Cu-BTC/UiO-66	TBAB	12 bar, 8 h, 60 °C	84	-	>99	[33]
UiO-66/Cu-BTC	TBAB	12 bar, 8 h, 60 °C	91	-	>99	[33]

[a] $mmol_{product}/mmol_{catalyst}$

The catalytic potentials of Cu-HKUST-1 and Cu-MOF in cyclic carbonate formation were investigated in 2019 via density functional theory (DFT), by Hu *et al*. [34] and Li *et al*. [17] in two different studies. Both studies showed that the rate-determining step of the reaction mechanism is the ring-opening of the epoxide. Furthermore, Hu *et al*. [34] reported that among the co-catalysts studied, the bromide anion was predicted to be the most effective due to it

having the lowest activation energy barrier in the ring-opening step (F^- 29.18 kcal mol^{-1} > Cl^- 16.13 kcal mol^{-1} > I^- 13.73 kcal mol^{-1} > Br^- 12.40 kcal mol^{-1}).

Although the use of co-catalysts such as TBAB lead to efficient catalytic systems and increase the reaction yield, recycling TBAB from the reaction mixture is difficult, due to the high solubility of the ammonium salts in the reaction mixture solution. In addition, halide anions can cause ferrous metal corrosion, which is an issue for large-scale industrial implementation. To try to overcome this issue, various metal ions, including zirconium, zinc and copper, which can act as active catalytic sites in the catalyst, have been incorporated into MOFs.

Zanon *et al*. [35] in 2017, prepared zinc and cobalt doped ZIFs (zeolitic imidazolate frameworks, a subclass of MOFs), using zinc nitrate tetrahydrate ($Zn(NO_3)_2.4H_2O$), cobalt nitrate hexahydrate ($Co(NO_3)_2.6H_2O$), and 2-methylimidazole. The synthesized Zn-Co-ZIF-67 catalyst could form cyclic carbonates without a co-catalyst or solvent and was reported to give excellent conversions for ECH (100%) using 7 bar of CO_2 at 100 °C for 2 hours using 50 mg of catalyst with 9 mmol of substrate. In this case, the authors proposed that the metal center coordinates to the oxygen atom of the epoxide, thus activating the epoxide (Figure 8).

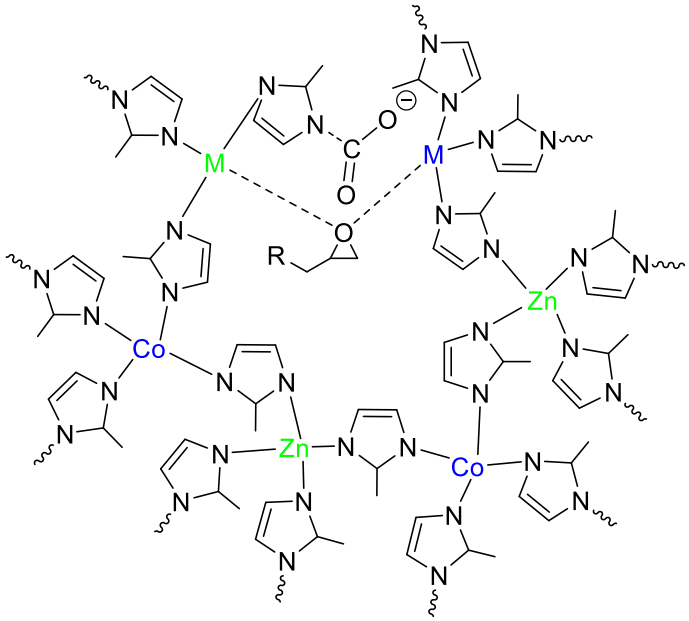


Figure 8. Proposed reaction mechanism for the formation of cyclic carbonates from ZIF catalyst Zn-ZIF-67. Both zinc and cobalt metal sites coordinate to the epoxide [35].

In 2018, Wu *et al*. [36,37], Song *et al*. [38] and Zhang *et al*. [4] reported the use of MOFs doped with metals, such as potassium, cobalt, manganese and zinc, in cyclic carbonate synthesis. These metals were used because they provide unsaturated cations, which can serve as Lewis acidic sites, and thus remove the need for a co-catalyst to activate the epoxide. This, combined with the presence of basic nitrogen atoms in the MOF structure, promotes the CO_2 activation step in the reaction mechanism (Figure 9).

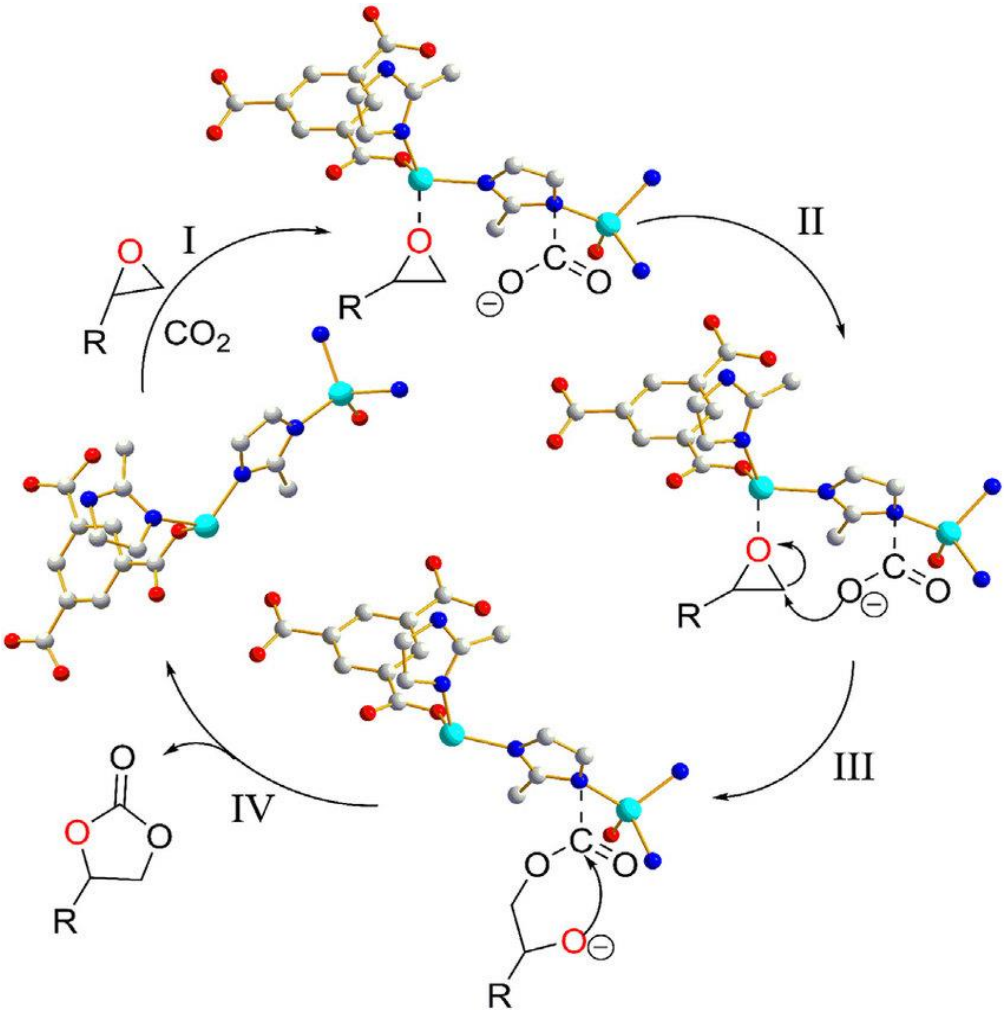


Figure 9. Cyclic formation using Zn-doped MOFs. Adapted with permission from Wu *et al*. [37].

In 2020, Xiang *et al*. [39] discovered that the dual-ligand ZIF "ZIF-8-90" (ZIF-8 and ZIF-90 combined), was an effective catalyst for cyclic carbonate formation. The dual ligand ZIF displayed greater catalytic properties, giving 90% ECH conversion, compared to the mono-ligand ZIFs. Both acidic and basic sites, located at the external surface of the ZIF catalyst, were responsible for cyclic carbonate formation. It was proposed in the reaction mechanism, that the

basic nitrogen atom sites adsorb CO_2, whereas the acidic unsaturated zinc sites adsorb the oxygen of the epoxide. Despite the great activity of this catalyst, non-ambient conditions were required (20 bar of CO_2).

In 2019, a review of MOF-based catalysts for the direct catalytic conversion of CO_2 to cyclic carbonates under mild conditions was written by Huh [40]. Huh summarized that for the majority of MOFs reported in the literature, Lewis or Brønsted acidic sites on the catalyst accelerated the reaction. Furthermore, bifunctional acid-base MOF catalysts demonstrated good recoverability and stability, and could be recycled approximately 5-10 times.

The direct incorporation of bromide nucleophiles into MOFs was also reported in this review. By incorporating bromide anions in close proximity to the Lewis acid metal center, no co-catalyst was required for cyclic carbonate formation and reactions could be performed under mild conditions (1 bar of CO_2 and room temperature for 24 h). However, conversions and product selectivity were very low, compared to when co-catalysts were used.

Cui and co-workers [41] also published a review of MOF-based heterogeneous catalysts, focusing on their use in the reactions of CO, CO_2 and CH_4. According to the authors, there are three different types of MOFs, each with different catalytic sites: (1) MOFs with structural defects; (2) MOFs with catalytically active metal nodes; and (3) MOFs with functional linkers. All of these MOFs have been studied as catalysts for forming cyclic carbonates from epoxides and CO_2.

In Cui's review [41], it was noted that MOFs with structural defects, and thus a high abundance of Lewis basic sites on the surface of the catalyst, are extremely promising candidates for CO_2 conversion. On the other hand, MOFs with Lewis or Brønsted acidic metal nodes (termed as secondary building units, SBUs, often incorporating organic ligands as short-range bridges between metal centers) could also activate the epoxide molecule. These catalysts however cannot act as one-component catalysts, as an extra Lewis basic component (and therefore co-catalyst) is required to ring-open the epoxide ring.

The third type of MOFs reported in the review were MOFs with functional linkers. The introduction of Lewis basic functional groups such as amines ($-NR_2$), pyrazoles and uncoordinated nitrogen atoms as organic linkers, created one-component catalysts with Lewis acidic metal centers and Lewis basic

organic linker sites. These groups combined could therefore synergistically activate and ring-open the epoxide. The majority of MOF-based catalytic systems with structural defects or active metal nodes required Lewis basic co-catalysts to optimize epoxide conversions.

MOFs with dual catalytic metal centers on the other hand are active even in the absence of a co-catalyst, but require high-pressure and/or high-temperatures. As a result, MOF-based heterogeneous catalysts are very competitive with some of the most active catalysts reported in the literature. Creating MOF catalysts that can synthesize cyclic carbonates synthesis without a reaction solvent and/or co-catalyst under mild conditions however still remains a challenge.

2.3. Metal Oxides

Metal oxides have been tested as catalysts for cyclic carbonate formation as they contain both acidic and basic sites and have redox properties, which can create defects and thus oxygen vacancies, in the catalyst. These oxides constitute the largest family of catalysts in heterogeneous catalysis [42]. Recently, many metal oxides have shown promise as catalysts for cyclic carbonate synthesis and can be synthesized easily, by various techniques with great reproducibility.

Tambe and Yadav [43] reported that tetragonal zirconia (t-ZrO_2), doped with La^{3+} cations (La–ZrO_2), promotes styrene carbonate (SC) formation from styrene oxide (SO) and CO_2. The La^{3+} cations can substitute Zr^{4+} cations in the metal oxide framework, resulting in oxygen vacancies which act as strong Lewis basic sites [44]. Carbon dioxide can be adsorbed by these sites, while SO is adsorbed onto the acidic zirconia sites. This catalyst is therefore predicted to follow the Langmuir–Hinshelwood–Hougen–Watson (LHHW) model (Figure 10).

In 2018, Rasal *et al*. [45] also showed that incorporation of lithium cations into a MgO lattice significantly increased catalytic activity. Prior to lithium doping, the conversion of ECH into cyclic carbonate was approximately 30%, whereas after doping it increased to 96%, using 0.75% (w/w) of lithium and carrying out reactions at 130 °C, and 30 bar of CO_2 for 4 hours. Furthermore,

catalyst basicity increased after lithium doping, as characterized by temperature-programmed desorption of CO_2, and it was hypothesized that this increase in basicity was associated with oxygen vacancy generation.

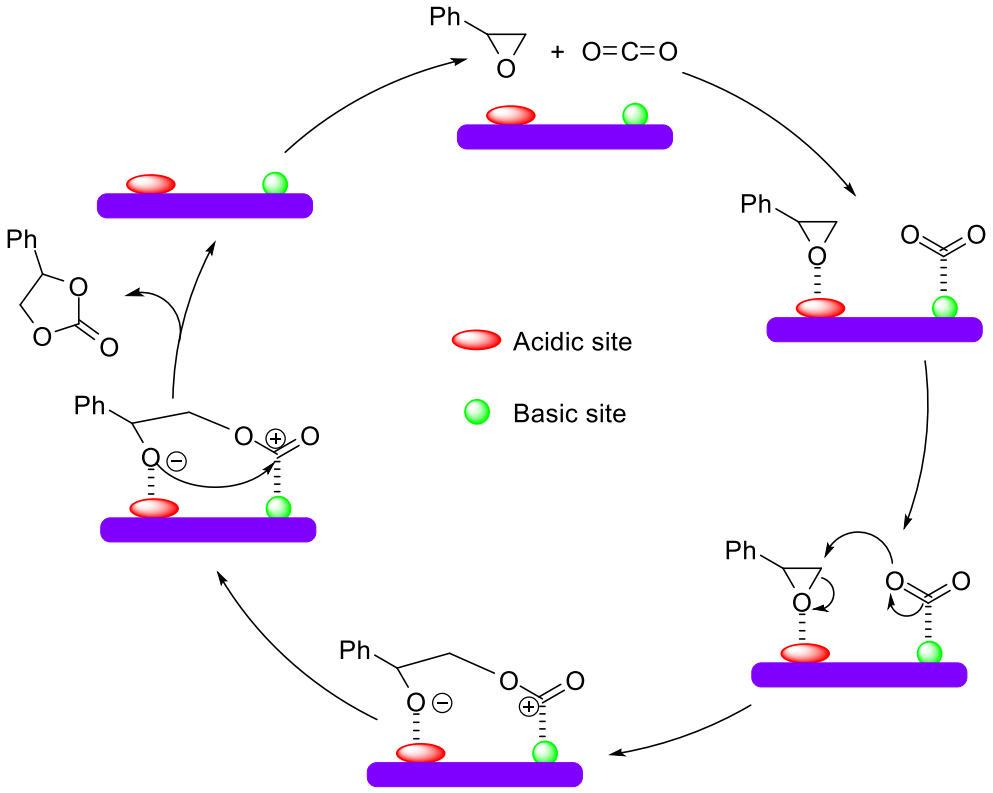


Figure 10. Proposed reaction mechanism of the formation of cyclic carbonates using the La–ZrO_2 catalyst [43].

In 2018, Chowdhury *et al.* [46] also reported the use of a MgO nanomaterial for the synthesis of cyclic carbonates via CO_2 fixation with a wide range of epoxides under ambient reaction conditions, with TBAB as a co-catalyst. The catalyst showed good reactivity, with an isolated yield of 99% reported for the conversion of ECH into the corresponding cyclic carbonate under mild conditions (1 bar of CO_2 and room temperature after 4 hours). The authors proposed in the reaction mechanism that the magnesium cations act as Lewis acid sites and thus activate the oxygen of the epoxide. Furthermore, the bromide anion from TBAB promotes the ring-opening step. It was also proposed that the O^{2-} sites of MgO act as Lewis basic sites, which in turn activate the CO_2 molecule (Figure 11).

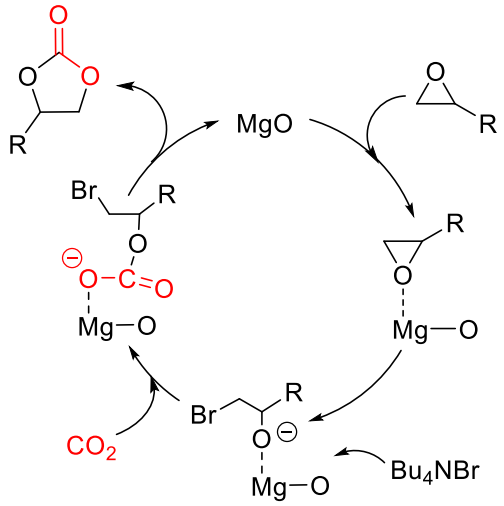


Figure 11. Proposed reaction mechanism for the conversion of CO_2 and epoxides into cyclic carbonate, using a MgO nanomaterial and TBAB [46].

In 2019, Zhao *et al*. [47] reported for the first time the use of boron trioxide (B_2O_3) as an effective metal-free heterogeneous catalyst, for the production of cyclic carbonates from epoxides and CO_2. In this work, the authors used bromide anions from TBAB as the nucleophile to promote the ring-opening step. It was proposed that the boride sites of the catalyst acted as Lewis acids in the reaction mechanism. Under optimum reaction conditions (100 °C for 2 hours with 20 bar of CO_2 and using 2.5 mol% of B_2O_3), an isolated yield of 90% was reported for PC. When the authors used just 0.5 mol% of B_2O_3 catalyst, it was found that pre-treating the catalyst by ball milling for 2 hours, increased the yield of PC considerably from 40 to 95%. The pressure required for this system however was much higher (20 bar) compared to other works cited in this research area.

In 2019, Middelkoop *et al*. [48] reported the first use of 3D printers to manufacture new heterogeneous catalysts for the conversion of CO_2 into cyclic carbonates. In this paper, the authors compared the catalytic activity between CeZrLa and CeZrLa/GO (GO: graphene oxide) nanocomposites, created by a continuous hydrothermal flow synthesis (CHFS) process and 3D printing, respectively. It was found that the optimal catalyst contained a polymer/powder ratio of 54 wt% of polymer (made from aqueous solution of methyl cellulose) and 42 wt% of the nano-powder, mixed with a small amount of lubrication additive (4 wt%) using a planetary centrifugal mixer (Figure 12). No organic solvents were required to prepare this catalyst.

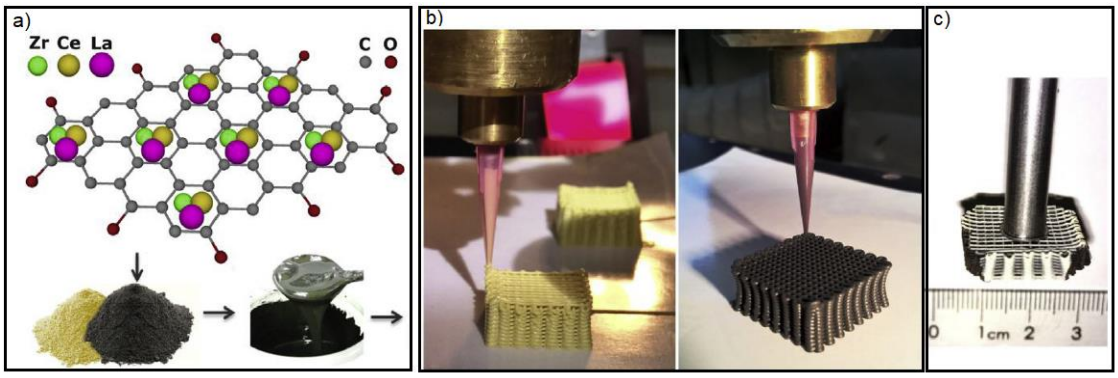


Figure 12. a) Simplified structure of CeZrLa (yellow powder) and CeZrLa/GO (black powder) nanocomposites, synthesized by a CHFS process; b) 3D printing of the CeZrLa and CeZrLa/GO catalysts through a 600 mm nozzle in stacked layers of fibers; c) The CeZrLa/GO catalyst mounted onto an impeller shaft of a stirred batch reactor cell.
Adapted with permission from Middelkoop *et al*. [48].

The GO-supported catalyst exhibited higher surface areas (128 m^2/g) compared to the control material without the GO support (109 m^2/g) and the standard 2D CeZrLa material (92 m^2/g). Furthermore, the 3D printed structures showed greater PO conversion (94%) compared to the 2D CeZrLa powder (89%). This greater catalytic activity was believed to be due to the greater surface area of the 3D printed catalyst, enabling better accessibility of the epoxide and CO_2 to the catalyst's active sites.

Overall, metal oxides are promising heterogeneous catalysts for cyclic carbonate synthesis. In addition, they can be easily synthesized, separated from the mixture reaction and their performance can be easily modified, by changing structural aspects, such as morphology, particle size and doping.

2.4 Carbon-based

In order to try and meet the challenge of converting epoxides into cyclic carbonates in a potentially more sustainable and metal free process [49], attention has turned towards using carbon-based materials. Carbon materials have a high surface area, good chemical and mechanical stability and high conductivity, features that allow for easy transformation and production of materials with different shapes and dimensions.

Recently, 2D carbon based materials have received huge attention as alternative catalysts, due to their large surface areas and excellent reactivity

[50,51]. Pure carbon materials are most often inert in the conversion of CO_2, as for example in the reaction to reduce carbon dioxide. However, by inserting heteroatoms, such as nitrogen, into these materials, basic sites are introduced into the matrix, increasing CO_2 absorption, stability and facilitating their use as catalysts [52].

One material that has been researched extensively is graphite carbon nitride (g-C_3N_4), which is often used for CO_2 absorption, due to the presence of CO_2 absorbing amine and guanidine groups [53–55]. Goettmann *et al*. first reported in 2007 that mesoporous g-C_3N_4 could activate a CO_2 molecule and convert benzene and CO_2 into phenol [56]. This report sparked other researchers to study using g-C_3N_4 as a catalyst for carbon dioxide utilisation [57–60].

In 2017, Samanta and Srivastava [61] prepared a bifunctional catalyst from g-C_3N_4 for cyclic carbonate synthesis, esterification and transesterification reactions. The authors reacted g-C_3N_4 with H_2SO_4(aq) at different concentrations (20%, 40% and 60%). Temperature programmed desorption analysis of NH_3 and CO_2 from g-C_3N_4 identified the bifunctional character of the catalyst, as it revealed the presence of acidic (-SO_3H) and basic (-NH_2) sites. For cyclic carbonate formation, the authors observed that catalyst acidity influenced catalytic activity, as the catalyst prepared with 60% H_2SO_4(aq), S-CN(UTU)-60, and thus with the greatest number of acidic sites, was the most active. Terminal epoxides ethylene oxide (EO), PO and ECH were tested as substrates. By investigating the reaction conditions required to convert ECH into cyclic carbonate, the optimum reaction conditions were found to be, 50 mg of catalyst for 63 mmol of epoxide, at 10 bar of CO_2 and 100 °C with a minimum reaction time of 4 hours required for high conversions. Whilst high conversions and selectivities were obtained for EO and ECH (more than 90%), a more moderate conversion (63%) was reported for PO. Although this catalyst is sustainable and simple to make, a much wider range of epoxides could have been tested with this catalyst, including internal epoxides.

The justification for the observed catalytic activity was the presence of both acidic and basic sites, allowing the simultaneous activation of epoxide and CO_2, respectively, thus promoting the insertion of CO_2 and the consequent formation of cyclic carbonate. This acidic g-C_3N_4 catalyst was also more active

than standard zeolite, magnesium oxide and magnesium/aluminium hydrotalcite.

Also in 2017, Biswas and Mahalingan [62] explored for the first time the synergistic effect of using g-C_3N_4 with TBAB to convert epoxides into cyclic carbonates. By simply using 50 mg of g-C_3N_4 and 1.8 mol% of TBAB with respect to epoxide (13.7 mmol) at 1 bar of CO_2 and 105 °C for 20 hours, 100% conversion of epoxide to cyclic carbonate was reported for ECH, SO, phenyl glycidyl ether (PGE) and allyl glycidyl ether (AGE). Relatively low conversions were however reported for other epoxides including 1,2-epoxy hexane, 1,2-epoxy octane, 1,2-epoxy-9-decene, and no ring-opening of the internal epoxide cyclohexene oxide (CHO) occurred. Only conversions were reported rather than isolated yields of the cyclic carbonate products. Catalyst recycling tests demonstrated no loss in activity after 7 cycles.

Control tests performed with these reagents as separate components always resulted in conversions under 40%. The authors therefore propose that g-C_3N_4 and TBAB work in a cooperative manner. The authors suggest that the primary and secondary g-C_3N_4 amino groups activate the epoxide ring via hydrogen bond formation, which thus increases the electrophilicity of the epoxide carbon atoms. This makes the carbon atom more susceptible for nucleophilic attack by the bromide anion of TBAB, causing the epoxide to ring-open and thus initiating the conversion of epoxide into cyclic carbonate (Figure 13).

In 2018, Zhang *et al*. [63] studied the use of graphene oxides (GOs) as green and inexpensive alternative catalysts for the conversion of epoxides into cyclic carbonates under atmospheric pressures of CO_2. Styrene oxide (SO, 5 mmol) was used to screen this catalyst (using only 5 mg of catalyst) against various reaction conditions, and it was determined that the optimal reaction conditions were 140 °C and 1 bar of CO_2 for 6 hours with 4 mL of *N,N*-dimethylformamide (DMF). This catalyst was also more active than standard activated carbon and acetylene black (aka carbon black). Despite reporting high selectivities >95%, conversions of SO were moderate at 75% and lower than other metal free or metal based catalytic systems. Considering that only 5 mg of catalyst was however required, 75% conversion is impressive. The catalyst was

also recyclable was tested with conversions and selectivity keeping fairly consistent, only dropping from 90.3 to 87.5%, after four cycles.

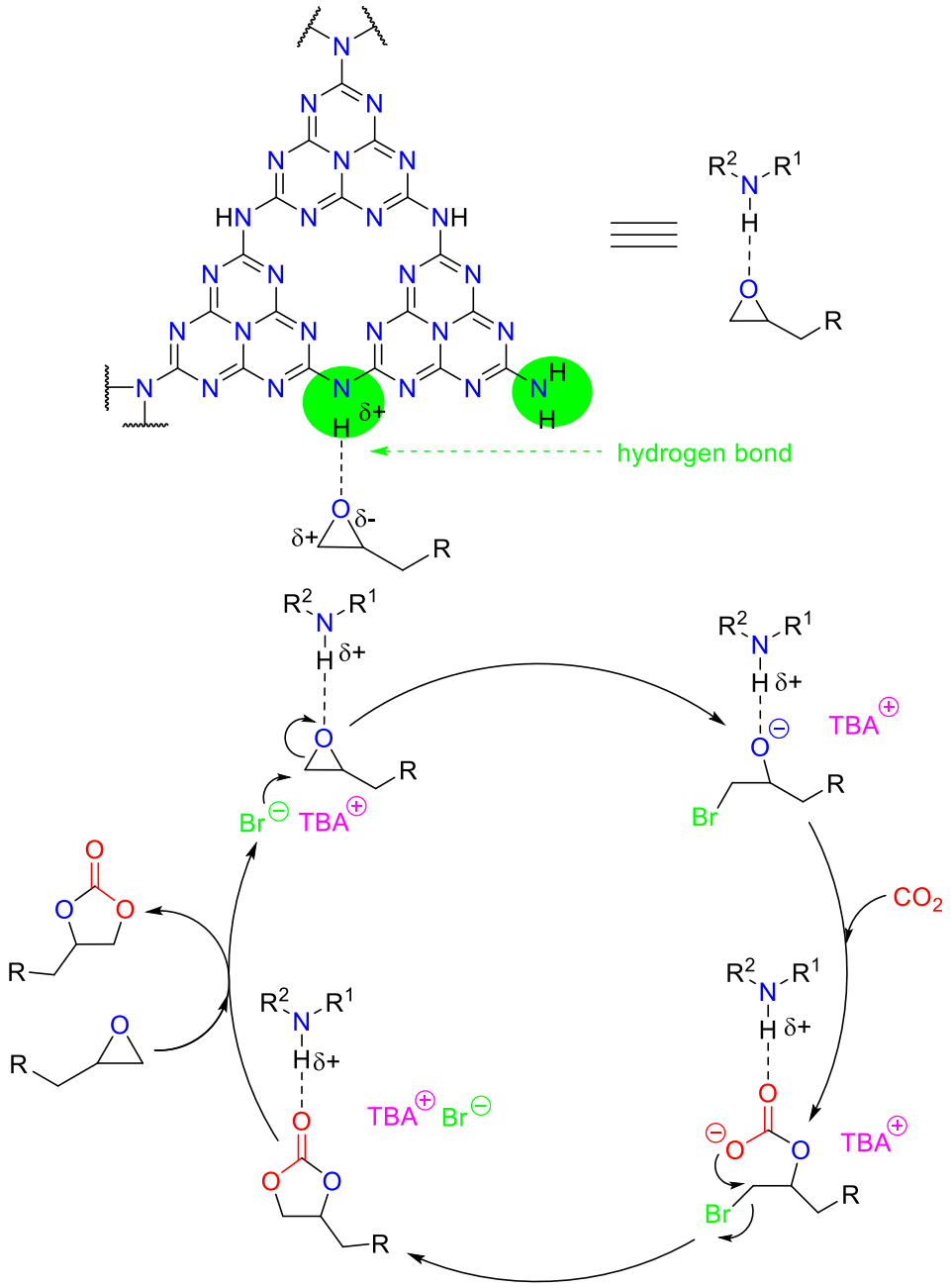
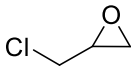
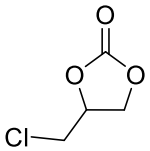
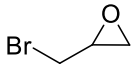
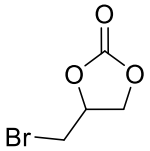
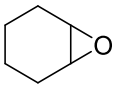
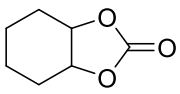
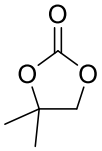
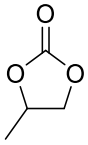


Figure 13. Proposed mechanism for the g-C_3N_4 and TBAB catalyzed conversion of epoxides and CO_2 into cyclic carbonates [62].

The authors proposed that CO_2 activation occurs in the reaction solvent DMF and that quaternary C-OH groups on the GO surface are responsible for epoxide activation. This was further supported by the observations that no increase in conversion occurs with an increase in CO_2 pressure when DMF is used in the reaction; and oxidised GOs, with more oxygen functionality, were

more active than reduced GOs. The conversion of other terminal epoxides to cyclic organic carbonates was also tested, with conversions and selectivity's greater than 90% reported (Table 2). Ideally, this reaction would work in the presence of a much greener solvent than DMF, as DMF is soon to be restricted under REACH guidelines. This system also struggled to convert CHO into cyclic carbonate, but could convert some simple internal epoxides into cyclic carbonates.

Table 2. Cyclic carbonate formation from GO catalysed cycloaddition reactions between CO_2 and epoxides [63].

Entry	Substrate	Product	Temp. (°C)	Time (h)	Conv. (%)	Sel. (%)
1			100	12	>99.9	95.6
2			100	12	>99.9	96.1
3			140	10	39.7	99.8
4			140	10	89.9	96.3
5			140	10	96.6	98.3

Reaction conditions: Substrates (5 mmol), DMF (4 mL), 2.5 mg of GO and 1 bar of CO_2.

Inspired by the successful application of numerous carbon-based materials with oxygenated groups on the surface, Vidal *et al*. [64] decided in 2019 to study the catalytic ability of biochar (carbon-rich solids produced by the pyrolysis of biomass at low oxygen concentrations and temperatures). The authors prepared their catalysts from two different types of wood, one soft and the other hard, which were treated with nitric acid to produce oxidized biochar with carboxyl groups on its surface. In this study, it was reported that 10 mol%

of TBAB (with respect to epoxide) was required as a co-catalyst. In the absence of TBAB, the biochar catalysts showed no conversion of PO to PC. By using 200 mg of catalyst, 68 mmol of PO and 10 mol% of TBAB, at 100 °C and 20 bar of CO_2 for 16 hours, conversions of 91% were reported for PO. This catalyst gave moderate conversions for other simple terminal epoxides, such as SO, glycidol and ECH, but low conversions for CHO (<22%).

Both soft (ox-bc_{sw}) and hard (ox-bc_{hw}) wood oxidized materials gave similar conversions, which were unaffected when different types of wood were used to make the catalysts. Non-oxidized analogous materials (bc_{sw} and bc_{hw}) only gave 40% and 38.3% conversion, respectively, highlighting the importance of oxygen groups in the catalyst. It was also found that the catalyst ox–bc_{hw} was recyclable, showing no loss of activity after five cycles [64].

In 2019, Wang *et al*. [65] produced a single atom catalyst (SAC), a catalyst support with metals dispersed throughout on an atomic level, by doping graphene with zinc (NG-aZnN). The authors hypothesized that the NG-aZnN catalyst could potentially activate epoxides and initiate the reaction efficiently, in the presence of different alkyl ammonium salts which could cooperatively lead to cyclic carbonate formation, and were the first to test these catalysts in cyclic carbonate formation. In the initial studies, the transformation of PO and CO_2 into PC was investigated. The optimized reaction conditions were found to be 15 mg of NG-aZnN (0.12 mol% of zinc with respect to epoxide) for 20 mmol of epoxide under 10 bar of CO_2 at 120 °C for 3 hours. When screened with numerous ammonium halide salts, it was found that this catalytic system was most active in the presence of tetraheptylammonium bromide (THPAB, $(nC_7H_{15})_4NBr$, 0.5 mol% with respect to epoxide), with increases in the alkyl chain lengths of the co-catalyst also leading to an increase in carbonate yield. Using these parameters, the authors obtained 98% isolated yield and 99% selectivity in the conversion of PO to PC.

An impressive range of epoxides were tested (10 in total) including terminal and internal epoxides, with >98% yields reported for all terminal epoxides and reasonable yields reported for internal epoxides (39-67%). Although this catalyst is not strictly metal free, the isolated yields and selectivities reported with such low metal loading are impressive.

2.5 Organic Polymer supports

An emerging type of porous materials are porous organic polymers (POPs), which have gained attention as useful materials for gas storage, pollutant removal and heterogeneous catalysis [67–69]. POPs are promising CO_2 absorbents. Since they can be prepared via a molecular building block (MBB) approach, which allows the adjustment of the chemical composition, surface area and pore size, as well as shape and functionality of the material, they can become stable materials with a strong affinity for CO_2. Factors such as high thermal and chemical stability enables these materials to also be used in strenuous reaction conditions if required, and therefore they often exhibit high catalytic activity and long durability [66].

The flexible synthetic routes used to make POPs allow their structures and porous properties to be elegantly fine-tuned by carefully selecting the desired building blocks of the POP at the molecular level [70,71]. Simultaneously, desired catalytic components can also be homogeneously embedded into POPs to enhance the catalytic activity and durability of the POP [72,73]. In this context, CO_2 attracting groups and catalytically active sites can be easily incorporated, to facilitate CO_2 adsorption and thus catalytic transformation.

In 2017, Zhong *et al*. [74] studied an imidazolium- and triazine-based POP with a chloride counter anion (IT-POP-1) as a catalyst in the conversion of ECH and CO_2 into cyclic carbonate, using only 0.1 mol% of IT-POP-1 at 10 bar of CO_2 and 120 °C for 10 hours. Under these conditions, the authors achieved yields and selectivities greater than 98%, without the need for a solvent or co-catalyst. To understand the influence of the chloride counter anion, the authors synthesized and studied two other POPs, with an iodide (IT-POP-2) and hexafluorophosphate anion (IT-POP-3), respectively. Cyclic carbonate (gas chromatography, GC) yields obtained using IT-POP-2 and IT-POP-3 were 89% and 33%, respectively, both with a selectivity of 99%. The low catalytic activity of IT-POP-3 is attributed to the low nucleophilicity of the hexafluorophosphate anion, which is much lower than that of an iodide anion. The superior result for IT-POP-1 was attributed to the synergistic effect of this catalyst containing the largest Brunauer-Emmett-Teller (BET) surface area and the strong

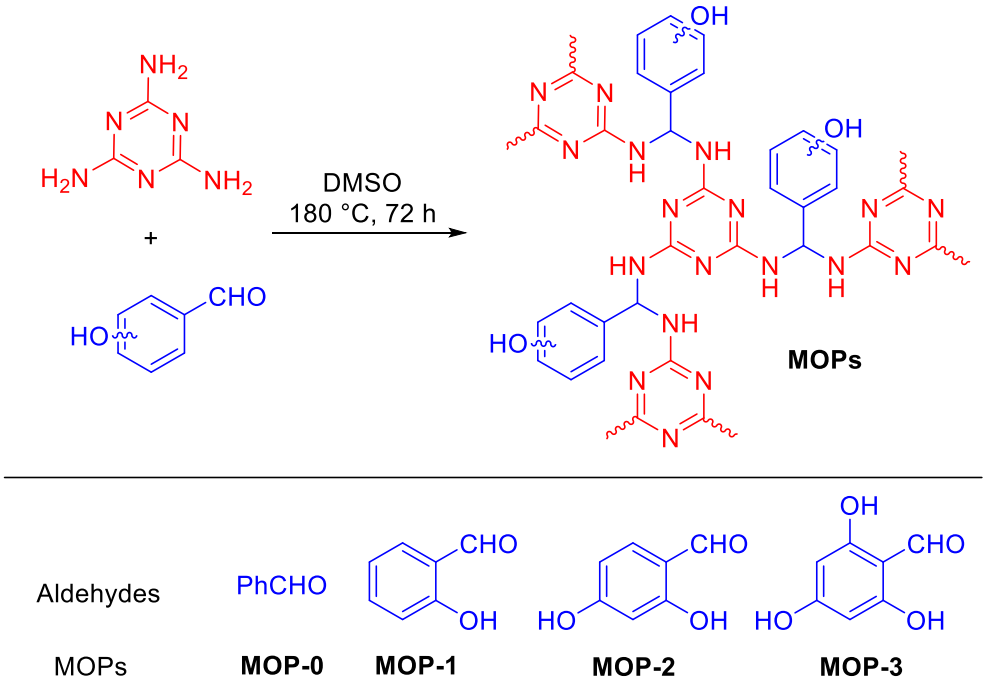
nucleophilicity of the chloride anion. These characteristics facilitate faster mass transfer and a greater capacity for nucleophilic attack, compared to the other catalysts. Catalyst IT-POP-1 was tested against nine terminal epoxides, with moderate to excellent yields reported. This catalyst could also be recycled, with no loss in catalytic activity and selectivity reported after 5 cycles.

The authors suggest that the activity of IT-POP catalysts overall, is due to the porosity of the materials and the presence of imidazole and triazine in the catalyst increasing the adsorption capacity of the catalyst, and thus the ability to activate CO_2. As the imidazole and triazine groups in the catalyst framework contain hydroxyl groups, the author hypothesized that cyclic carbonate formation is promoted synchronously by hydrogen bond formation occurring between these hydroxyl groups and the epoxide, and then the chloride anion in the pores of the catalyst ring-opening the epoxide. This synergistic effect thus accelerates the rate-determining step of the reaction. Whilst this system is impressive and can be used at low catalytic loadings, the synthesis of these catalysts requires the unsustainable solvent DMF and they were not tested in the conversion of internal epoxides. Isolated yields of the carbonates from the reaction mixtures were also not reported.

In 2017, Zhang *et al*. [75] prepared mesoporous organic polymers (MOPs) via a one-pot polycondensation of melamine and monoaldehydes, for the adsorption and conversion of CO_2 into cyclic carbonates. Four catalysts were prepared from benzaldehyde and its hydroxylated derivatives: MOP-0 to MOP-3 (Scheme 1).

These catalysts were tested against ECH (10 mmol), using 50 mg of MOP catalyst at 10 bar of CO_2 and 100 °C for 24 hours, with 2 mmol of biphenyl added as an internal standard. A decrease in catalytic activity was reported as the number of hydroxyl groups increased; the GC yields were 89% (MOP-0), 86% (MOP-1), 81% (MOP-2) and 58% (MOP-3). Although MOPs have typically been reported to convert epoxides into cyclic carbonates via hydrogen bond formation, it was concluded by the authors that an increase in hydroxyl groups caused a reduction in material porosity. This therefore increased the difficulty in diffusing the epoxide to the active sites. The most active catalyst, MOP-0, could be used up to 5 times without any loss in catalytic activity. This catalytic system

was screened only against terminal epoxides (11 in total) and sometimes required 5 mol% of KI or TBAI to achieve excellent conversions.



Scheme 1. Synthetic route used to make MOP catalysts: MOP-0 to MOP-3 [75].

In 2017, Verma *et al*. [76] developed a nitrogen-rich polymeric catalyst, termed as cyanuric–urea polymer (CUP). This catalyst was formed by heating cyanuric chloride and urea to 140 °C under solvent free conditions, in a cross-linking mechanism (Figure 14).

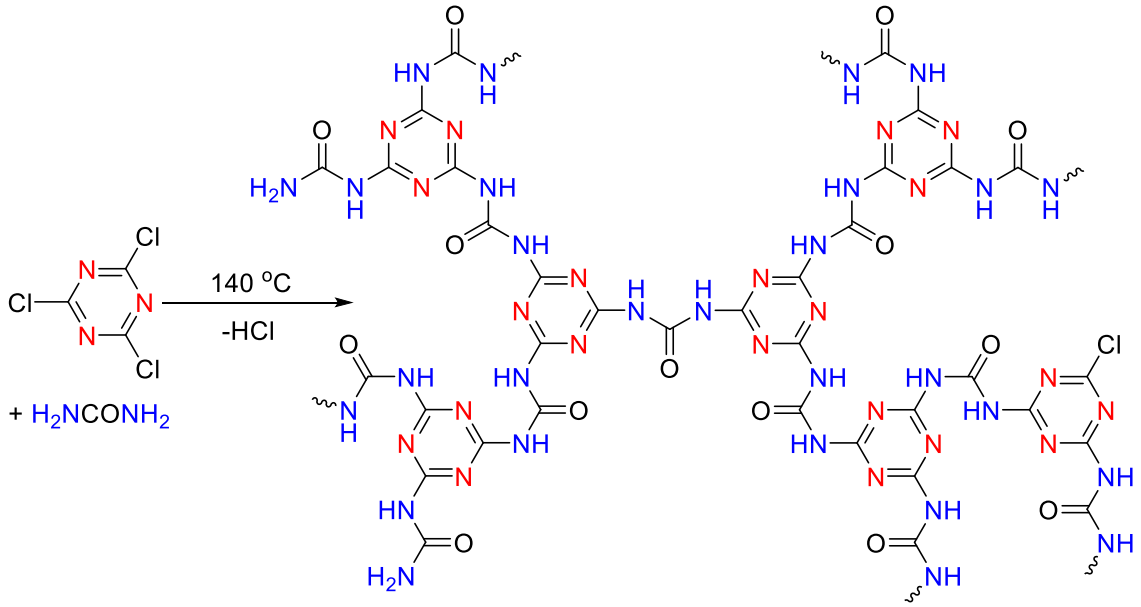
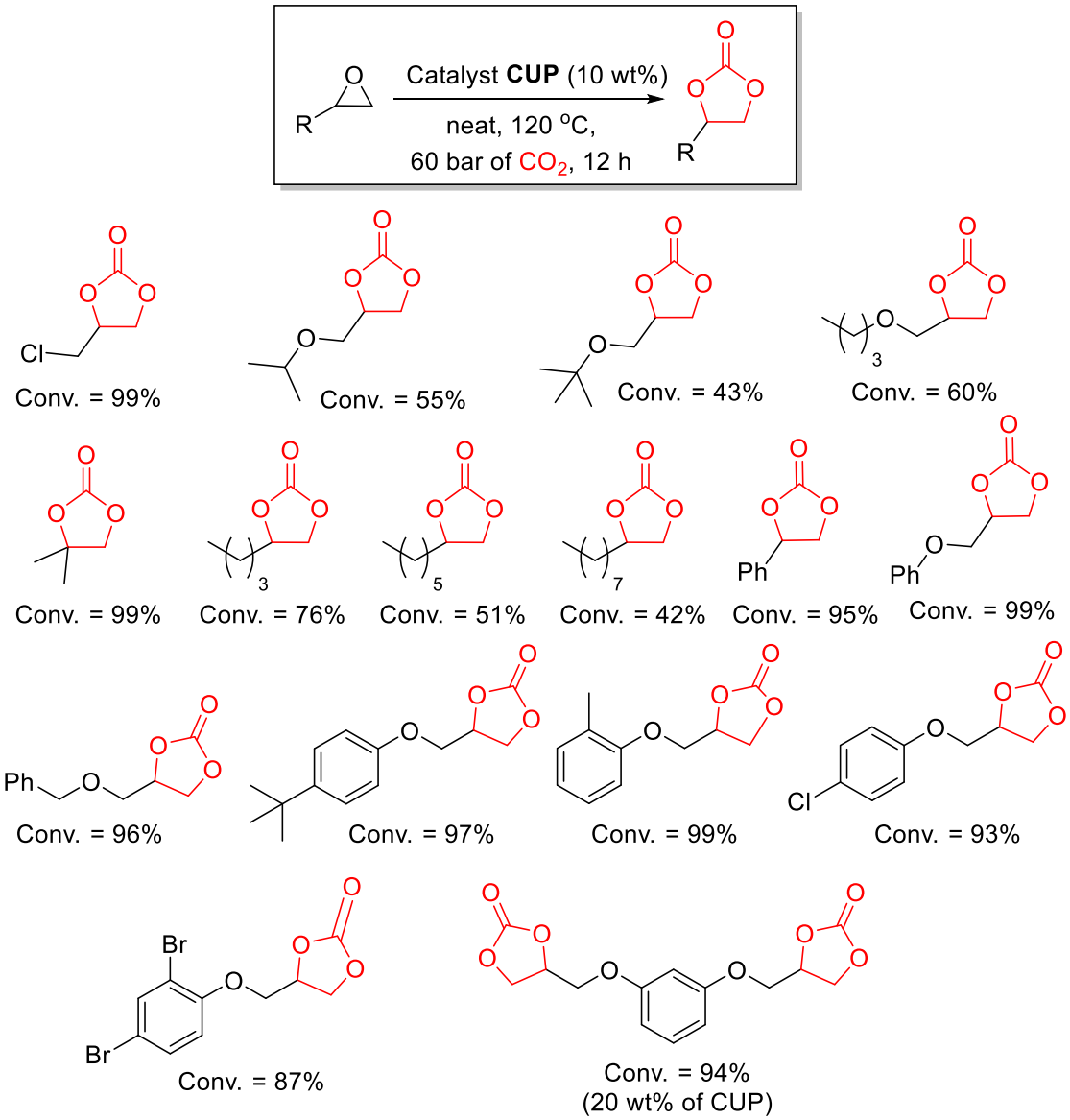


Figure 14. Synthetic route to make the CUP catalyst [76].

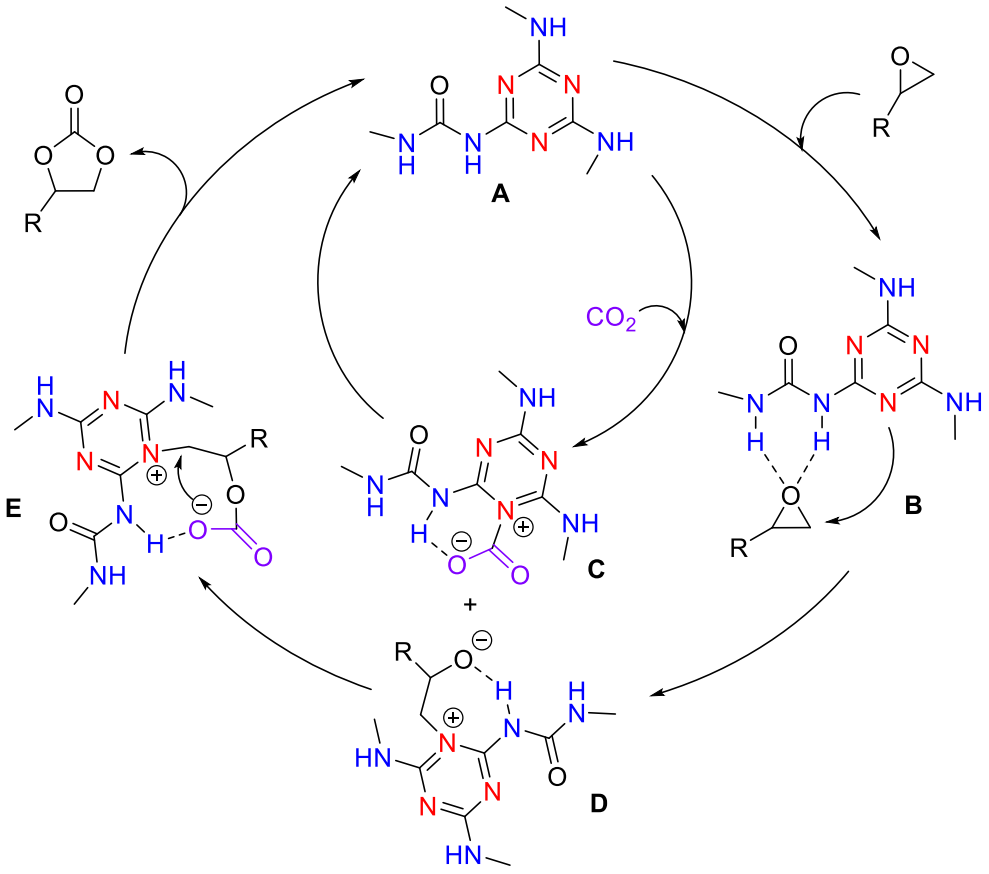
The prepared material was initially tested in the conversion of PO to PC, using 5-20 wt% of CUP catalyst at 30-120 °C and 20-60 bar of CO_2 for 12 hours. Among the conditions evaluated, the highest conversions were obtained using 10-20 wt% of catalyst, 120 °C and 60 bar of CO_2 for 12 hours, giving 99% conversion for PO. The conversion of 16 other epoxides to cyclic carbonates with CUP was also reported (Scheme 2). The CUP catalyst could also be used in 7 reaction cycles without any loss in catalytic activity. Conversions were determined from ^{1}H NMR analysis of the crude reaction mixtures.



Scheme 2. Substrate scope of catalyst CUP, in the cycloaddition reaction of aromatic, aryloxy and aliphatic terminal epoxides with CO_2 [76].

In the same study, Verma *et al*. [76] proposed that the reaction mechanism is driven by the two different nitrogen environments present in the

catalyst (Scheme 3). It was hypothesised that the non-aromatic nitrogen groups activate the epoxide via hydrogen bonding (intermediate B), and the aromatic nitrogen groups activate CO_2 due to their basic nature (intermediate C). Intermediate B is then converted into intermediate D, which can react with intermediate C and then undergo ring-closure via intermediate F to from cyclic carbonate. Despite the promise of this catalyst, the conditions used are quite harsh and energy intensive compared to other catalysts reported in the literature. No isolated yields are reported for this catalytic system and no internal epoxides were tested. On a positive note, this catalyst was used on a large scale, converting 10 g of epoxide in each test, which is not always straightforward.



Scheme 3. Proposed mechanism for the cycloaddition of CO_2 to epoxides using the CUP catalyst [76].

In 2017, Jawad *et al.* [77] developed a highly bifunctional, solvent-stable, porous bromide aminopropyltrimethoxysilane (Br/APS) grafted ZrO_2 polyamide-imide (PAI) hollow fiber catalyst, Br/APS/Zr-PAIHF. This bifunctional catalyst consists of a porous ZrO_2-PAI hollow fiber support, with acidic and basic Lewis

species and nucleophilic bromide anions immobilized in the catalyst support. Under the optimum reaction conditions of 30 mmol of SO, 50 mL of acetonitrile or DMF, 300 mg of catalyst, 20 bar of CO_2 pressure and 160 °C for 6 hours, 100% conversion of SO into SC was achieved with 100% selectivity. ICP elemental analysis of the catalyst after use in three reactions revealed that the Br/APS/Zr-PAIHF catalyst maintained its structure and chemical composition, with low bromide leaching reported. Bromide free versions of this catalyst also led to no conversion, highlighting the importance of the bromide anion in the reaction mechanism. Although this catalyst was never tested in recycling experiments, these results indicate that catalyst recycling is feasible. It would also be interesting to see how active this catalyst is in ring-opening other epoxides.

Ravi *et al*. [78], in 2017, synthesized porous aromatic polymers which were functionalized with ethylenediamine (CBAP-1(EDA)) and then complexed with Zn^{2+} (EDA-Zn) or Co^{2+} (EDA-Co) cations (Figure 15).

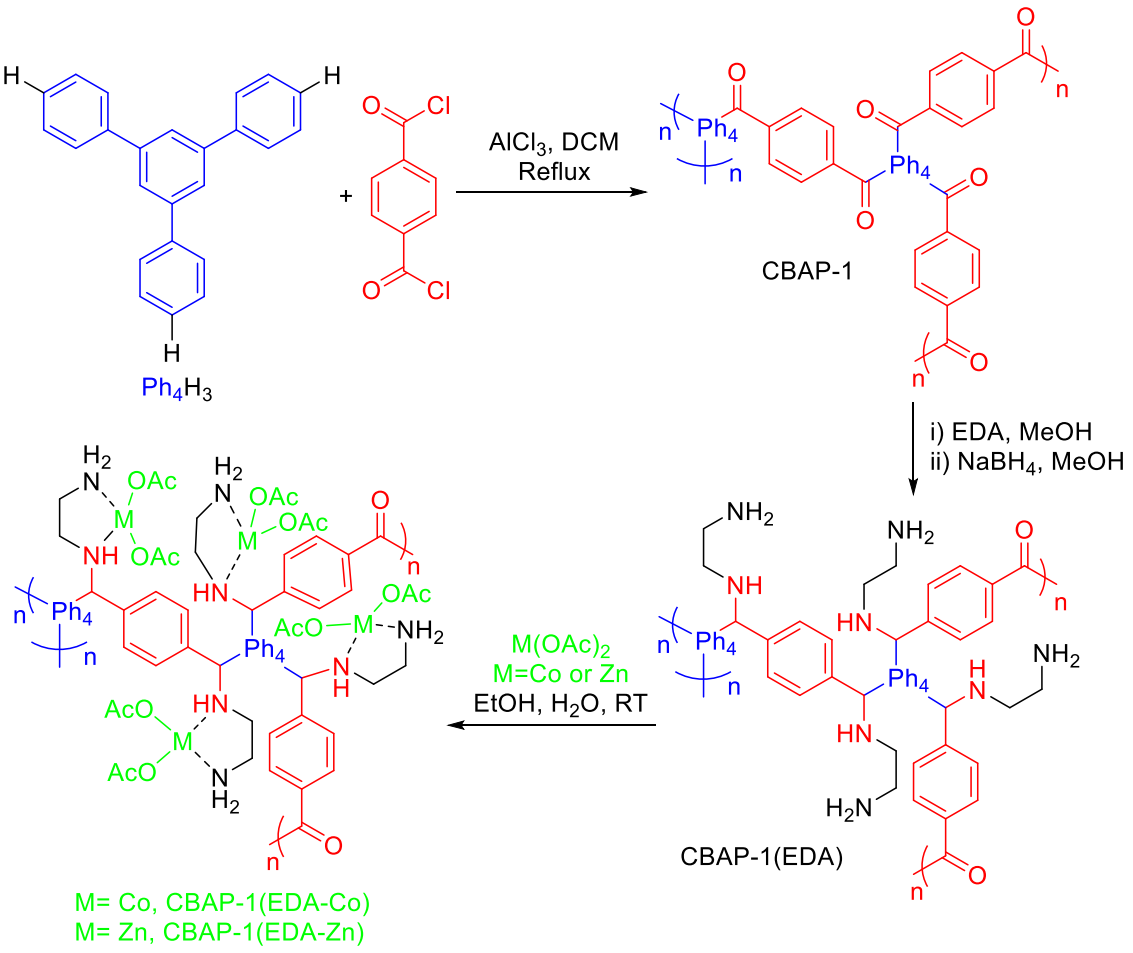
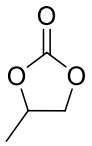
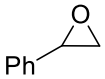
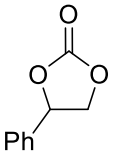
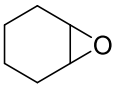
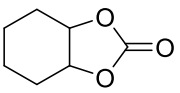
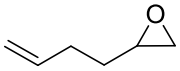
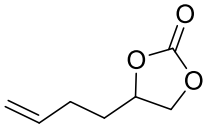
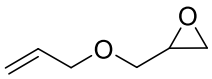
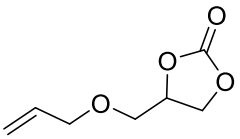


Figure 15. Synthesis of CBAP-1(EDA-Zn) and CBAP-1(EDA-Co) [78].

In the conversion of ECH to cyclic carbonate, CBAP-1(EDA) showed high conversion and selectivity, both 99%, using 40 mg of catalyst with 20 mmol of ECH and 10 bar of CO_2 at 130 °C for 4 hours. This reaction did not require a co-catalyst, solvent or metal. The catalytic activity of CBAP-1(EDA) could be increased when used in conjunction with nucleophiles; as when CBAP-1(EDA) was used with 1.8 mmol% of TBAB, conversions of 98% were reported at the lower temperature of 80 °C, using 10 bar of CO_2 for 8 hours.

Table 3. Conversion of epoxides and CO_2 into cyclic carbonates, using CBAP-1(EDA) and CBAP-1(EDA-Zn) [78].

Entry	Substrate	Product	Temp. (°C)	Time (h)	Sel. (%)	Yield (%)[d]
1			130[a]	4	99	98
2			25[b]	36	95	81
3			60[c]	48	98	34
4			25[b]	36	98	89
5			25[b]	36	97	84

Reaction conditions: Epoxide (20 mmol). [a]CBAP-1(EDA) (40mg) and 10 bar of CO_2; [b]CBAP-1(EDA-Zn) (40 mg), TBAB (1.8 mol%) and 10 bar of CO_2; [c]CBAP-1(EDA-Zn) (40 mg), TBAB (1.8 mol%) and 1 bar of CO_2; [d]Isolated yields.

When tests were conducted with the metal-doped samples, CBAP-1(EDA-Zn) and CBAP-1(EDA-Co) with 1.8 mol% of TBAB, conversions of 96% and 91%, with selectivity to carbonate of 98% and 97%, were reported respectively. These impressive conversions could be achieved in 36 hours using 10 bar of CO_2 at room temperature. In recycling experiments, CBAP-

1(EDA) showed no loss in catalytic activity after 5 cycles, at 130 °C for 4 hours. Catalyst CBAP-1(EDA-Zn) also showed no significant loss of activity after 5 cycles, in the presence of TBAB at 25 °C for 36 hours.

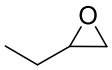
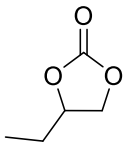
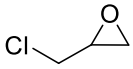
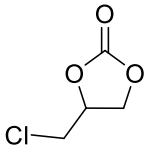
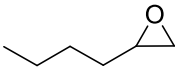
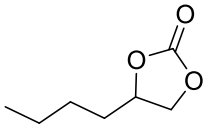
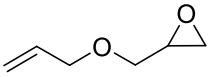
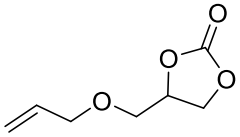
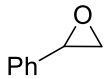
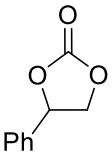
The authors tested catalysts CBAP-1(EDA) and CBAP-1(EDA-Zn) in the formation of cyclic carbonates from other epoxides (Table 3), demonstrating the applicability of this catalyst to convert numerous substrates. Whilst this catalyst was effective at converting some terminal epoxides, more substrates could have been tested and a low conversion was reported for the internal epoxide cyclohexene oxide, especially compared to other catalytic systems.

In 2018, Ma *et al*. [79] prepared a bifunctional porous organic framework (POF) heterogeneous catalyst, doped with bromide anions from pyridine-based ionic liquids (POF-PNA-Br^-). The authors sought to prepare a bifunctional metal-free environmentally friendly heterogeneous catalyst, to convert epoxides and CO_2 into cyclic carbonates without the need for a co-catalyst. They proposed that by employing carboxylic acid groups as Brønsted acid sites, and the bromide anion as nucleophilic sites, this catalyst alone could form cyclic carbonates. By using 50 mg of POF-PNA-Br^- for 30 mmol of PO, with 1 bar of CO_2 at 40 °C for 48 h, an isolated yield of 98.2% was reported for PC. Catalyst POF-PNA-Br^- could be used in up to 3 cycles with no significant loss in catalytic activity.

The POF-PNA-Br^- catalyst was also effective against other terminal epoxides, under the same reaction conditions used to transform PO into PC. The yields obtained for some substrates were not as impressive as other catalysts reported in the literature, especially for SC at just 52% (Table 4). A wider substrate scope could have been tested and no tests were performed with internal epoxides. Considering though that a low catalytic loading of catalyst was used with no co-catalyst, these conversions are significant.

The proposed reaction mechanism begins with the acidic Brønsted carboxylic acid groups activating the epoxide, followed by nucleophilic attack of the bromide anion causing the epoxide to ring-open. Insertion of CO_2 then occurs, followed by ring closure to form cyclic carbonate.

Table 4. Substrate scope of cyclic carbonate formation using catalyst POF-PNA-Br^- [79].

Entry	Substrate	Product	Yield (%)[a]
1			91.7
2			94.1
3			81.2
4			77.1
5			52.4

Reaction conditions: Epoxide (30 mmol): catalyst (50 mg), 1 bar of CO_2 and 40 °C for 48 h.
[a]Isolated yields.

In 2018, Ravi *et al.* [80] prepared a hydroxylamine-anchored covalent aromatic polymer (CAP-DAP) via a Friedel-Crafts benzoylation reaction, by reacting *p*-terphenyl and trimesoyl chloride together with $AlCl_3$, followed by functionalization with 1,3-diamino-2-propanol (Figure 16). This CAP-DAP catalyst (40 mg) could form cyclic carbonate from ECH (20 mmol) but gave a low conversion of only 8% without a co-catalyst, at 60 °C with 1 bar of CO_2 for 12 hours. When screened with different co-catalysts: tetrabutylammonium chloride (TBAC, *n*-Bu_4NCl), TBAB, TBAI and KI, (at 2 mol% with respect to epoxide), TBAB was the most active co-catalyst achieving 98% conversion and 99% selectivity, at 1 bar of CO_2 at 60 °C for 12 hours. The catalytic system of CAP-DAP and TBAB could be recycled and did not show any loss in activity after 6 cycles. The authors also tested this catalytic system in the conversion of PO, AGE, 1,2-epoxy-5-hexene and SO. All of the terminal epoxides tested showed high yields and selectivities: above 82% and 98% respectively. This

catalytic system was additionally tested in the conversion of one internal epoxide, CHO, but achieved only 13% yield and therefore seems only effective in ring-opening terminal epoxides

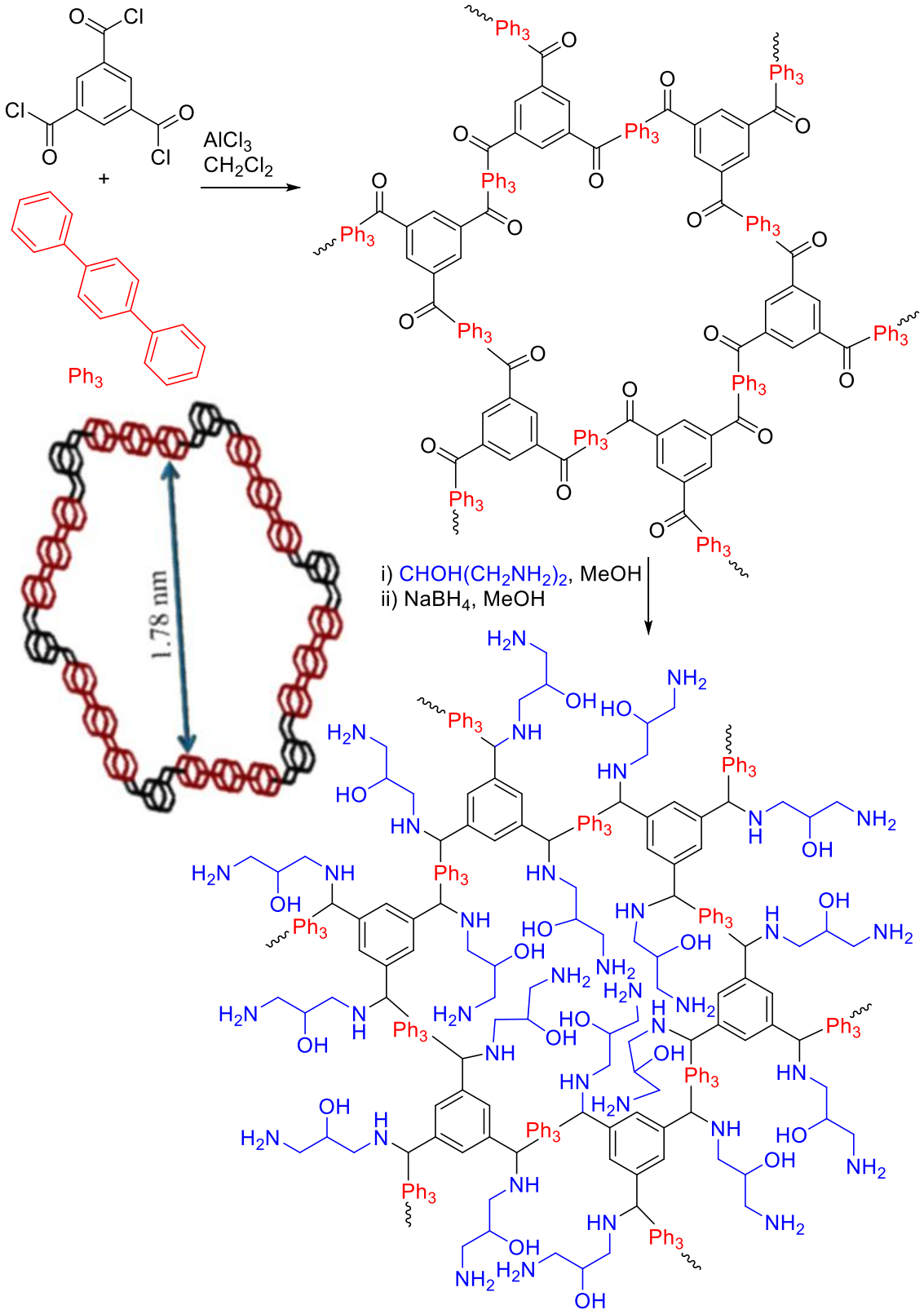


Figure 16. Synthesis of the CAP-DAP catalyst, followed by functionalization with 1,3-diamino-2-propanol. Adapted with permission from Ravi *et al.* [80].

The mechanism proposed by the authors begins with the hydroxyl group and the secondary amine group of the CAP-DAP catalyst, interacting with the oxygen of the epoxide via hydrogen bonding. This activated epoxide is then ring-opened by the nucleophilic bromide anion from TBAB, forming an alkoxide intermediate. The amine group also adsorbs CO_2 to form a carbamate, which is attacked by the alkoxide anion, followed by ring-closure, thus forming the cyclic carbonate (Figure 17).

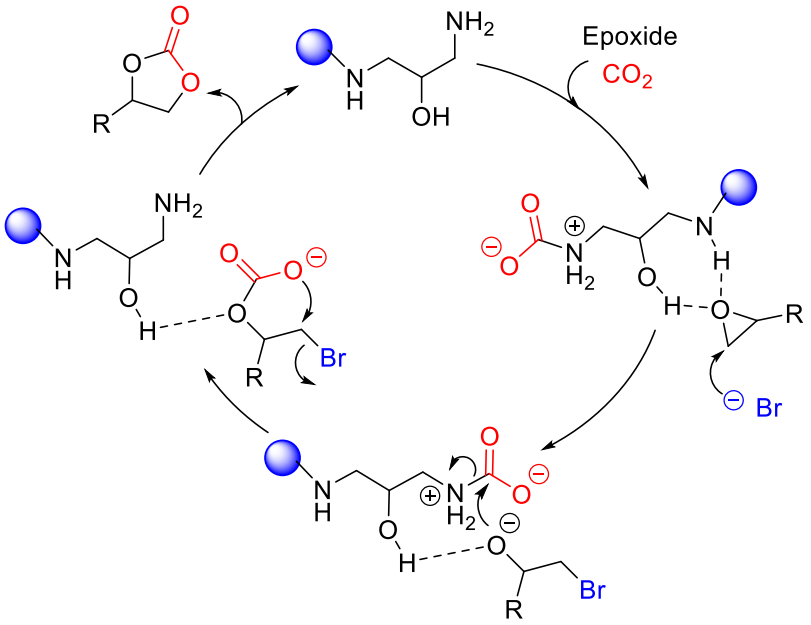


Figure 17. Proposed reaction mechanism for the conversion of ECH and CO_2 into cyclic carbonate using CAP-DAP catalyst [80].

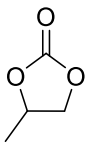
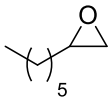
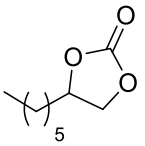
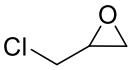
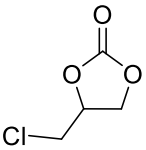
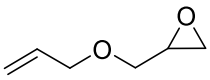
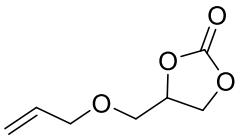
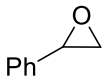
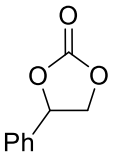
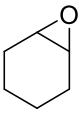
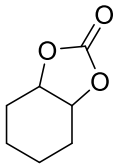
2.6 Zeolites

Zeolites, zeolite-based metal organic frameworks and amine-functionalized mesoporous materials have large surface areas combined with thermal and chemical stability. They also consist of large pores, which in terms of size can be easily adjusted. These materials can have many active functional sites, which can act as Brønsted acidic, Lewis acidic or Lewis basic sites. This makes these materials good adsorbents and catalysts for CO_2 absorption, either inside the pores or on the surface of the material [81].

In 2017, Bhin *et al.* [21] produced the zeolitic imidazolate framework ZIF-95 and tested it in the addition of CO_2 to epoxides. The material was prepared by a solvothermal route, using zinc nitrate tetrahydrate and 5-chlorobenzimidazole (cbIM) in DMF. The catalyst was initially tested in the

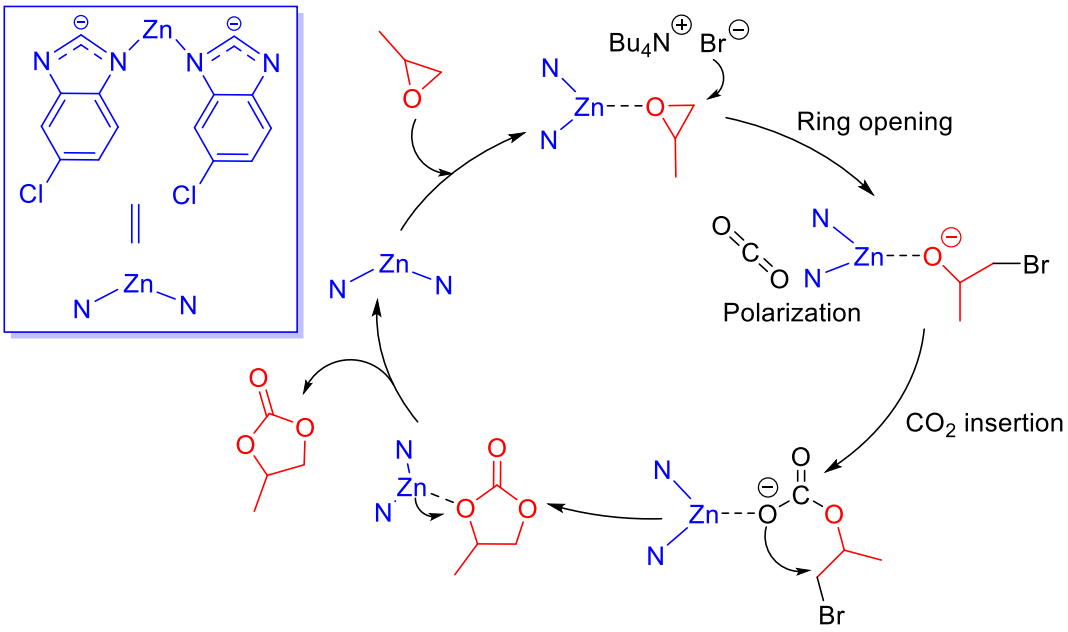
conversion of PO into PC. In the study, the authors evaluated catalytic loading of the co-catalyst TBAB and ZIF-95, temperature, CO_2 pressure and reaction time to obtain optimum conversions. The optimized conditions were 0.4 mol% of both ZIF-95 and TBAB, at 12 bar of CO_2 and 80 °C for 2 hours (using 18.6 mmol of epoxide). Under these conditions, 83.2% conversion for PO was achieved with a selectivity greater than 99%. The ZIF-95 catalyst could be recycled five times, in the conversion of PO, with no significant loss in activity. Other epoxides were tested, with excellent selectivities reported in all cases, but low conversions were reported for SO and the internal epoxide CHO (Table 5).

Table 5. Synthesis of cyclic carbonates using catalyst ZIF-95 [21].

Entry	Substrate	Product	Conv. at 120 °C (%)	Selectivity (%)
1			83.2	>99
2			61.4	>99
3			76.5	>99
4			75.0	>99
5			56.9	>99
6			15.3	>99

Reaction conditions: 18.6 mmol of epoxide, 0.4 mol% of ZIF-95 and TBAB, 12 bar of CO_2, 2 h.

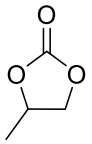
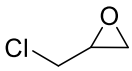
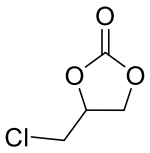
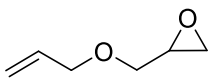
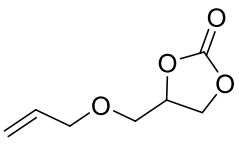
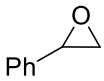
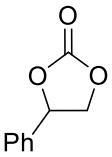
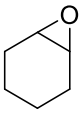
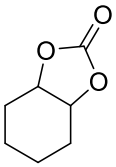
The mechanism for epoxide and CO_2 cycloaddition with ZIF-95 and TBAB was proposed to begin with the unsaturated zinc atom of ZIF-95 coordinating to the oxygen atom of the epoxide. The epoxide is then ring-opened by the bromide anion from TBAB, followed by CO_2 insertion and then ring-closure, with regeneration of the catalyst (Scheme 4).



Scheme 4. Mechanism of ZIF-95 and TBAB assisted CO_2-epoxide cycloaddition [21].

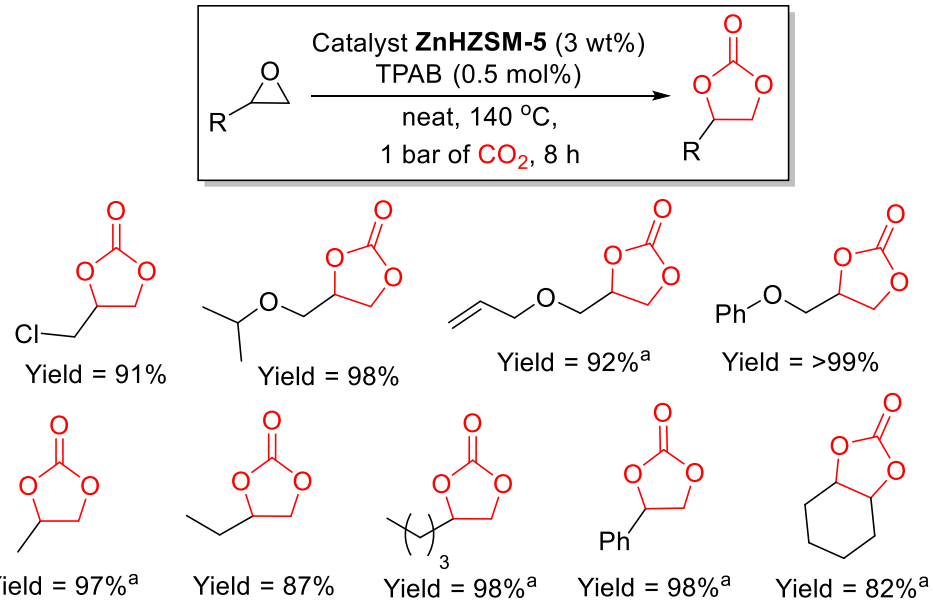
In 2018, Babu *et al.* [82] prepared zinc-based zeolitic imidazolium framework ZIF-71, using zinc acetate and 4,5-dichloroimidizole, for cyclic carbonate synthesis. The catalyst was tested in the conversion of different epoxides (ECH, PO and SO), using ≤ 0.6 mol% of catalyst at 12 bar of CO_2. High conversions were obtained at 120 °C and at room temperature, a feat which is not always easy to achieve in cyclic carbonate synthesis (Table 6). No co-catalyst was required to obtain these conversions. The ZIF-71 catalyst was recycled in the conversion of PO at 120 °C, maintaining high conversions over 6 cycles.

Table 6. Substrate scope of ZIF-71 catalyst [82].

Entry	Substrate	Product	Conv. at 120 °C (%)[a]	Selectivity (%)	Conv. at 25 °C (%)[b]
1			99	>99	98
2			95	>99	97
3			85	>99	86
4			75	>99	73
5			8	>99	10

[a]0.2 mol% of ZIF-71, 42.8 mmol of epoxide, 12 bar of CO_2 at 120 °C for 4 h. [b]0.6 mol% of ZIF-71, 42.8 mmol of epoxide, 12 bar of CO_2 at 25 °C for 24 h.

In 2018, Zhao *et al*. [83] developed a multifunctional heterogeneous zinc-modified catalyst, ZnHZSM-5, for the synthesis of cyclic carbonates under mild conditions. This catalyst was extremely effective in ring-opening many simple terminal epoxides but struggled with CHO (Scheme 5). This catalyst also required the co-catalyst tetra-*n*-propylammonium bromide (TPAB, nPr_4NBr) in order to obtain reasonable conversions. This ZnHZSM-5 catalyst gave higher yields than the standard HZMS-5 zeolite. It was therefore suggested that the multifunctional synergistic activation of the epoxide and CO_2 through the metal activated hydrogen groups in the catalyst ($ZnOH^+$), in the presence of bromide anions from TPAB, leads to a more effective catalyst.



Scheme 5. Substrate scope using ZnHZSM-5 catalyst. All yields quoted are isolated yields. [a]160 °C at 10 bar of CO_2 for 4 h [83]

We have studied ion-exchanged zeolite Y impregnated with metal halides as a heterogeneous catalyst for the synthesis of styrene carbonate. The best results were obtained with potassium iodide impregnated on potassium exchanged zeolite Y (KI/KY) and sodium iodide impregnated on sodium exchanged zeolite Y. Both these systems gave 100% yield of styrene carbonate at 100 °C and 50 bar CO_2 after 24 hours using an amount of zeolite containing 5 mol% of MI relative to styrene oxide [84]. Figure 18 shows the catalytic activity of KI/KY and KI in the production of styrene carbonate. It can be seen that the zeolitic system is significantly more active, achieving 100% yield within 6 hours, whereas KI required about twice this time to reach the same conversion. The impregnation of metal halides on zeolites has been previously used to ascertain the mechanism of ionic reactions inside the pores [85,86], suggesting a solvent-like behaviour for the zeolite system, which favours the stabilization of charge-separated transition states.

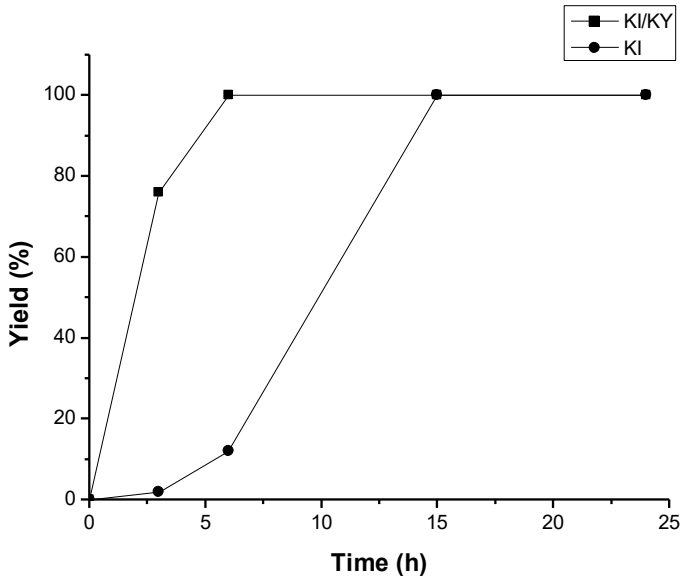


Figure 18. Yield of styrene carbonate against time in the reaction of CO_2 and styrene oxide at 100 °C and 50 bar CO_2 over KI/KY and KI (5 mol% of KI in both cases) as catalysts.

3. Conclusion

Overall, many heterogeneous catalysts have been successfully employed in the conversion of epoxides and CO_2 into cyclic carbonates, often at low catalytic loadings. The main challenges that still need to be overcome with these catalysts include obtaining good conversions for the more challenging internal epoxides, not just simple, sterically unhindered terminal epoxides, and obtaining reasonable conversions and yields under milder reaction conditions. Whilst these catalysts can, impressively, be employed with low metal loadings, co-catalyst loadings and sometimes without a co-catalyst, some catalysts still struggle to produce comparable conversions to metal-based complexes. The sustainability of some of these catalytic systems must also be improved, such as removing the need for toxic and unsustainable solvents like DMF. The future for these catalysts though is promising and they will continue to be an important field of research for promoting green and sustainable CO_2 utilisation.

Acknowledgements

The authors thank the Royal Society for International Collaboration Award IC170051. CJAM thanks CNPq and Faperj for fellowships.

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* of special interest
* * of outstanding interest

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